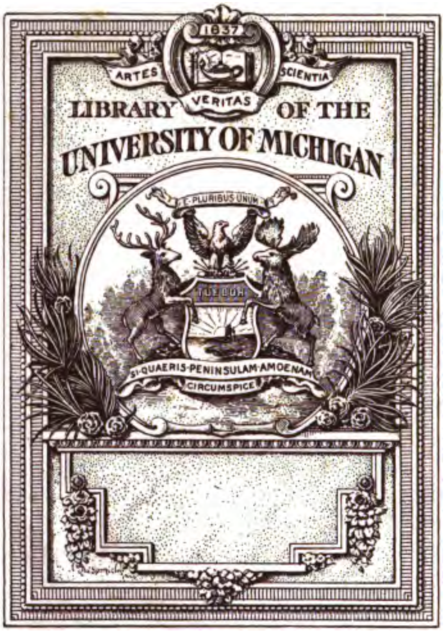
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MOLECULES

AND THE

MOLECULAR THEORY

OF

MATTER

BY

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PREFACE.

In the multiplication of popular books on scientific subjects, the molecular theory of matter appears to have been strangely neglected. None of the works available to American readers pretend to give a complete, connected account of what is known of the constitution of matter, and the student who wishes to learn the present state of the molecular theory has to seek his information in the occasional articles that are scattered through the scientific journals. Dr. Watson's *Kinetic Theory of Gases* (a new edition of which has been recently published) is far too difficult for the undergraduates in our scientific schools and colleges; Clausius's *Kinetische Theorie der Gase* (1889–91) has not yet been translated, nor has Meyer's *Kinetische Theorie der Gase*, so far as I am aware. Meyer's book is also out of print at present, although a new edition is in preparation. Lord Kelvin's delightful lecture on *The Size of Atoms* should be read by all students of physics, and it is now readily available, in the first volume of his *Popular Lectures and Addresses.* Crookes's classical papers on radiant matter should also be read; they are in the *Proceedings* of the Royal Society, beginning with the year 1874.

The present volume is an attempt to elucidate the elements of the molecular theory of matter as it is held to-day. It is based on a lecture delivered on the 12th of last February, before the Washburn Engineering Society, of the Worcester Polytechnic Institute. In preparing the manuscript for the printer a considerable number of alterations have been made, and much new material has been added, though the form of presentation has been preserved. Special care has been taken

to exclude all matter except that which has an immediate and evident bearing on *molecules;* otherwise this book would have been a treatise on physics. For this reason many exceedingly interesting theories and discoveries have been omitted or dismissed with slight mention — such, for example, as the investigations of Ostwald and others on solutions. It could hardly be expected that different men would agree on what should be passed over in this way, and it is likely that better judgment might have been used in many places. It is also likely that there have been many oversights and accidental omissions. In some cases important theories have been passed over because it was believed that they could not be adequately discussed without introducing considerable digressions upon the phenomena they are intended to explain. Professor Ewing's theory of magnetism is an example of this, and Clausius's theory of electrolysis has been dismissed with a bare mention, for like reasons.

Throughout this volume I have considered molecules in their physical aspect. There are numerous excellent works that discuss the chemical aspect of the molecular theory satisfactorily, of which the following may be particularly recommended: Meyer's *Modern Theories of Chemistry,* Remsen's *Theoretical Chemistry,* Ostwald's *Outlines of General Chemistry,* and Mendeleieff's *Principles of Chemistry.*

A. D. RISTEEN.

HARTFORD, CONN.,
September 1, 1894.

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MOLECULES AND THE MOLECULAR THEORY OF MATTER.

I. GENERAL CONSIDERATIONS.

The Molecular Hypothesis. — The molecular theory of matter, of which I shall speak to you this evening, declares that every mass of matter, however uniform and homogeneous and quiescent it may appear, is in reality composed of separate particles, each of which is in rapid motion. This proposition, although it may seem extravagant and improbable, has been forced upon us by a great variety of considerations, some of which I shall indicate to-night. It has been maintained, in one form or another, by various philosophers for the last 2300 years; but the reasoning of the ancients, on this subject at least, is so extremely subtle and nebulous that it has no value whatever for modern purposes. Nowadays the physicist requires us to state our assumptions very clearly, and to deduce from them their necessary consequences. He will then compare these consequences with the observed facts, and if the two are in perfect agreement he will accept our assumptions provisionally, and will believe in our theory until some one can show that we overlooked some absurd things that could be deduced from our premises, or until somebody brings forward another theory that is just as good as ours, or perhaps better. Although this modern spirit of doubt is rather hard on the "man with a theory," it is nevertheless quite logical. It prevents us from being swamped by a multitude of unsound theories, and enables us to distinguish the grain from the chaff. You will agree with me, therefore,

when I say that the real, healthy growth of the molecular theory of matter began when attempts were made to obtain *numerical results* from it.

Dalton's Contribution. — If this be admitted, I think we may say that the father of the present molecular theory was the English chemist, John Dalton. In the early part of the present century, Dalton called attention to the fact that when substances combine chemically, they do so in certain definite proportions. His reasoning was something like this: In 100 pounds of carbon monoxide there are 42.9 pounds of carbon, and 57.1 pounds of oxygen. In the same weight of carbonic acid there are 27.3 pounds of carbon, and 72.7 pounds of oxygen. No particular relations are discernible among these numbers; but Dalton found that if the same facts are stated in a different way, a very remarkable relation appears. Thus, suppose we calculate what weight of oxygen is combined *with each pound of carbon* in the two gases. In carbon monoxide we find that there are $\frac{57.1}{42.9} = 1.33$ pounds of oxygen to each pound of carbon, and in carbonic acid we find that there are $\frac{72.7}{27.3} = 2.66$ pounds to each pound of carbon. One of these numbers, you will see, is exactly twice the other; and we conclude that carbon can unite with oxygen in two proportions, the quantity of oxygen, per unit weight of carbon, being twice as great in one case as in the other. Dalton observed similar relations among other compounds,* and after turning the matter over in his mind he came to the conclusion that the facts could best be explained by assuming that matter consists of exceedingly minute, indivisible particles or atoms, each of which has a definite weight. When two bodies combine chemically, he conceived their atoms to come together in pairs, or in threes, or fours, according to the

* Dalton's theory first occurred to him, in fact, while he was studying the simpler compounds of carbon and hydrogen.

compound formed; and he devised symbols to represent the various elementary bodies and their compounds. Thus, in his notation,

Oxygen = ○	Carbon = ●
Hydrogen = ⊙	Nitrogen = ⦶

As water was the only compound of oxygen and hydrogen known to him, he represented it by the symbol ○⊙, considering that in it the particles of oxygen and hydrogen were united in *pairs*. Taking the hydrogen atom as the unit, it follows that the weight of the oxygen atom must be 8; for experiment shows that in a given mass of water there is 8 times as much oxygen, by weight, as there is hydrogen. Carbon monoxide was represented by the symbol ○●, and since for each unit of its oxygen (by weight) this gas contains $\frac{3}{4}$ of a unit of carbon, it follows that the atomic weight of carbon is $\frac{3}{4}$ of that of oxygen. Hence the weight of the carbon atom is 6. Carbonic acid was represented by the symbol ○●○. Ammonia, being the only known compound of hydrogen and nitrogen, was represented by the simple symbol ⦶⊙; and as experiment shows that ammonia gas contains $4\frac{2}{3}$ times as much nitrogen as hydrogen, the atomic weight of nitrogen must be $4\frac{2}{3}$. I have given you a general idea of the *kind* of reasoning Dalton used; but in calculating the atomic weights I have made use of better experimental results than were available to him. A few of his own early determinations of the atomic weights are given in the following table:*

Element.	Atomic Weight.
Hydrogen - -	1.0
Nitrogen - -	4.2
Carbon - - -	4.3
Phosphorus -	7.2
Oxygen - - -	5.5

* These were published in 1805.

Dalton's fundamental conception was correct, although the numbers that he used to express the atomic weights of the elements were erroneous, and so also were many of his formulæ. We agree with him, however, in believing that the so-called "atomic weights" of substances are really the *true relative weights of their atoms;* the weight of the hydrogen atom being taken as unity.

Similarity of Molecules. — Dalton assumed that all the molecules of any one substance are alike; but I think this ought not to be admitted without some experimental evidence. Various methods for testing this assumption have been proposed, and while none of them are absolutely convincing, the general inference to be drawn from them is, that there is no sensible difference among the constituent particles of any given substance. I will tell you briefly of two of the methods of investigation that have been proposed. Graham's method consisted in passing pure hydrogen gas through a porous partition between two vessels. The first part of the gas that came through was collected and caused to pass through a second similar partition. The first portion that came through this partition was caused to pass through a third one, and so the process was continued until the hydrogen had passed through a considerable number of the partitions. The hydrogen from the last operation was compared with the original hydrogen, and no difference between the two could be distinguished. It was therefore considered that this gas, at least, is not a mixture of dissimilar particles; because if it were, such a process as I have described could hardly fail to make some sort of a selection from among them, and the final gas would then be different from the primitive one. Another and a more convincing method of investigating the point in question, was tried by Stas.* He determined the atomic weight of the same substance when prepared in different

* Stas, *Untersuchungen über die Gesetze der chemischen Proportionen.* (Aronstein's translation.)

ways, from different sources, and under different conditions of temperature; and he found that the results were indistinguishable from one another. He also found the atomic weights of the elements to be the same, from whatever compound they were determined. His work was so accurate that it is not likely that a change in the atomic weight of more than the hundredth part of one per cent would escape detection. Since there was no observable difference, we must conclude that the atomic weights of his different samples were all sensibly alike; and this indicates that the *molecules* of these substances were all alike, because otherwise we could reasonably expect a slight difference to be discernible when a substance was prepared from different sources, by different methods. From these and other investigations, we conclude that until some data tending to prove the contrary are produced, we may reasonably proceed on the hypothesis that all the molecules of any given pure chemical substance are identically alike.

Hypothesis of Avogadro. — Soon after Dalton's theory had been announced, it was observed that there are simple *volumetric* relations among *gases* when they combine. Thus it was noticed that 2 volumes of hydrogen combine with 1 volume of oxygen, to produce approximately 2 volumes of steam; that 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid gas; and so on. This being the fact, it was suggested by Avogadro in 1811, and independently by Ampère in 1813, that *all gases*, when under the same conditions of temperature and pressure, *contain the same number of molecules per unit of volume.* This assumption also explains the observed fact that the densities of gases are proportional to their molecular weights; for if w_1 and w_2 are the weights of the individual molecules of two gases, and N_1 and N_2 are the numbers of the molecules in a unit volume of these gases, respectively, then the weights of a unit volume of the two gases are $N_1 w_1$ and $N_2 w_2$, respec-

tively. Now the observed fact is, that these quantities are proportional to w_1 and w_2; and hence we have the proportion

$$N_1 w_1 : N_2 w_2 = w_1 : w_2$$

from which it follows that $N_1 = N_2$; that is, it follows that Avogadro's hypothesis is true. I do not know whether chemists at first received this hypothesis as the expression of an actual fact in nature, or merely as a sort of convenient working hypothesis. However this was, subsequent investigation has made it increasingly probable, until now we must accept it as an established fact.

Distinction between Molecules and Atoms. — Molecules may be defined as the smallest parts into which a given substance can be conceived to be divided, without changing its chemical character. An *atom* is not so easily defined. Up to this point, in fact, I have made no distinction between a molecule and an atom; but if we are to accept Avogadro's hypothesis, it becomes necessary to make a distinction at once. For if you will think about it a moment, you will see that if *one* cubic inch of hydrogen, containing n molecules, combines with *one* cubic inch of chlorine, also containing n molecules, to produce *two* cubic inches of H Cl, containing n molecules altogether, then the number of molecules *in each cubic inch* of the H Cl gas is only $\frac{n}{2}$; whereas Avogadro's law requires us to assume the existence of n molecules in each cubic inch. It follows, therefore, that when the H and the Cl combine, their molecules do not simply unite in pairs. There is no way, in fact, to explain the observed facts, unless we assume that the molecules of H and Cl are both *compound*, and that when these gases combine, their molecules split in two, half a molecule of the one then uniting with half a molecule of the other, to produce a whole molecule of H Cl. This is made plainer by the diagrams. Figs. 1 and 2 represent small and equal volumes of H and Cl, on the assumption that their molecules are simple; and Fig. 4 represents the H Cl

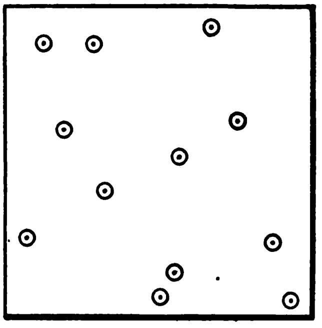


FIG. 1.—HYDROGEN MOLECULES.

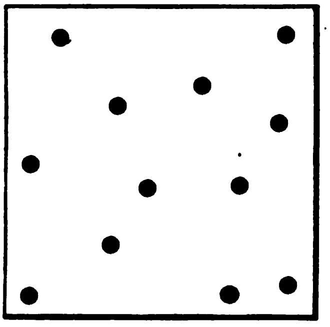


FIG. 2.—CHLORINE MOLECULES.

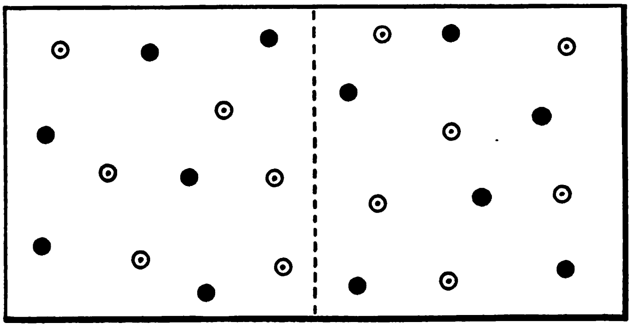


FIG. 3.—THE FOREGOING GASES MIXED.

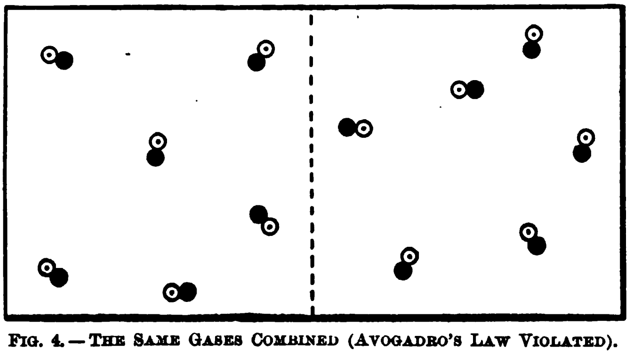


FIG. 4.—THE SAME GASES COMBINED (AVOGADRO'S LAW VIOLATED).

gas resulting from their combination. The space occupied by the H Cl gas is shown twice as large as that occupied by the component gases separately, because we know from experiment that when these component gases combine, the

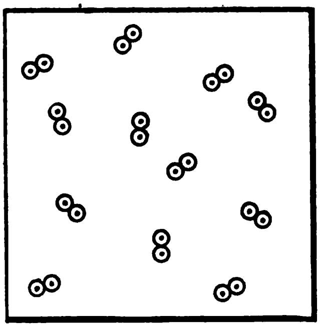


FIG. 5.—HYDROGEN MOLECULES.

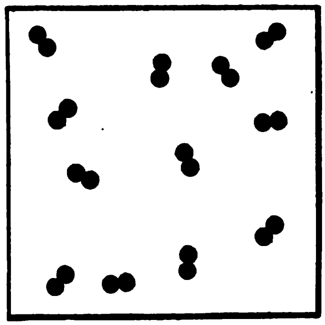


FIG. 6.—CHLORINE MOLECULES.

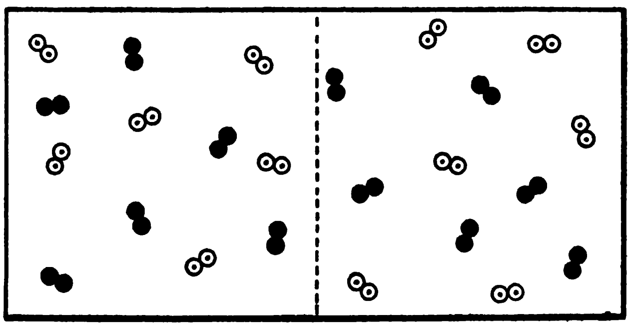


FIG. 7.—THE FOREGOING GASES MIXED.

volume of the result is equal to double the volume of either one of the constituents. But you will see that *the number of molecules per unit area* is only half as great in the H Cl as it is in either the H or the Cl; and this constitutes a violation of Avogadro's principle. Now if we conceive the molecules of H and Cl to be *compound*, as illustrated in Figs. 5 and 6,

we shall have no such anomaly. Fig. 8 represents the resulting H Cl, and you see that it fulfills Avogadro's law, as well as the observed fact of occupying two volumes. The compound nature of the molecules of the so-called elementary bodies is no mere logical figment; there is direct experimental evidence of its truth. It is known, for example, that many substances in the *nascent state,* just being set free from their compounds, are much more energetic in their chemical relations than they are under other circumstances; and it is hard to explain this fact by any theory that assumes the molecules of such substances to be simple. On the other

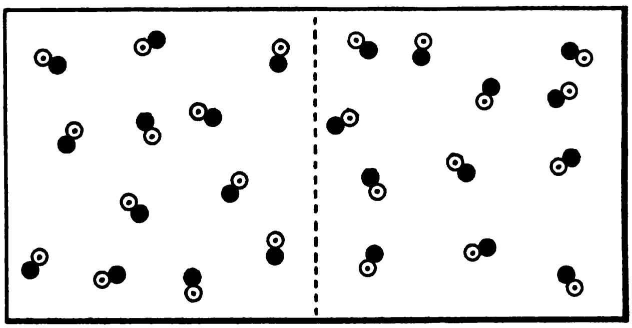


FIG. 8. — THE SAME GASES COMBINED (AVOGADRO'S LAW FULFILLED).

hand, the peculiar activity of nascent substances is quite intelligible if we assume that at the instant they are set free the parts of their molecules are not combined with one another to form what I may call *normal* molecules; for then the nascent substance could combine with other substances without first overcoming the internal forces that normally bind the parts of its own molecules together. In addition to the known activity of nascent substances, we have proof of the compound nature of molecules in the phenomenon known as *gaseous dissociation,* which is doubtless familiar to you if you have studied the properties of sulphur and sal ammoniac in your course in chemistry. I must caution you against sup-

posing that these sketches are intended as pictures of the actual molecules. They are simply *diagrams*, intended merely to aid you in understanding how Avogadro's law obliges us to conclude that the molecules of even the so-called elements are really compound bodies, capable of breaking up into atoms. Perhaps you will understand, now, what an atom is. An atom is one of the parts into which a molecule can be divided. We do not positively assert that a hydrogen molecule consists of only *two* atoms; but we know that when it divides it splits into *halves*, and in the absence of any evidence to the contrary we *assume* it to be di-atomic, though we must always remember that future research may require us to admit it to be tetratomic, hexatomic, or even more complex. In general, we assume for every substance the simplest molecular structure that is consistent with the observed facts. The facts now known regarding hydrogen, chlorine, and oxygen do not require us to assume more than *two* atoms to the molecule; but in some other bodies we do have to assume more than two — in sulphur, for example, we are required to admit that the molecule is at least *hexatomic*. We believe that the molecules of any one chemical substance are all alike; but we know that the atoms that compose these molecules are not alike unless the substance in question is an *element*. (Indeed, we do not positively know them to be alike, even in this case; but we assume them to be so, in the absence of any evidence to the contrary.) We know of only about 70 different kinds of *atoms;* but there are as many kinds of *molecules* as there are chemical substances; and it begins to look as though there is no limit to the number of these.

Classification of Bodies. — Leaving the historical aspect of the molecular theory, let us proceed to the consideration of its present state. We observe at the outset that bodies are divisible, physically speaking, into a certain small number of classes. We may, for present purposes, consider them as divisible into *solids* and *fluids;* fluids being further sub-

divided into *liquids* and *gases*. This classification is not all that could be desired, but it will serve. A *solid* body may be defined as a body capable of resisting a considerable shearing strain — a shearing strain being one which tends to cause one part of a body to *slide*, relatively to some other part. (See Fig. 9, in which S is a surface which has experienced a shearing strain greater than the material could sustain.) Solid bodies usually have considerable tensile strength also, and there are other properties peculiar to them, with which you are doubtless familiar. It is important to note that a solid does not yield *continuously* to a small deforming force. It resists deformation, and its resistance increases as the deform-

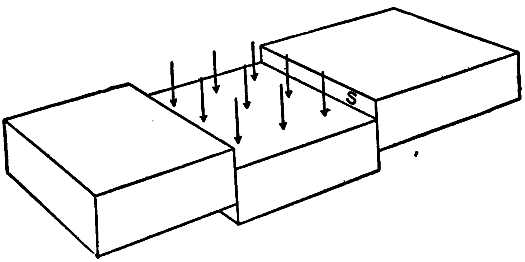


FIG. 9. — DIAGRAM ILLUSTRATING "SHEAR."

ation increases. A *fluid*, on the other hand, is a substance having almost no shearing strength, and offering very little resistance to forces that tend to change its *shape*. A fluid yields continuously to a deforming force, and a force that will deform it at all will deform it indefinitely, so long as it is allowed to act. Considering the subdivision of fluids into gases and liquids, we may say that a *gas* is a fluid that presses continuously and in every direction on the walls of the vessel containing it, and which follows them indefinitely if they retreat. A gas, if left to itself, tends to expand infinitely in every direction. A *liquid* is a fluid which does not follow the walls of the containing vessel if they retreat, and which has no tendency to expand infinitely if left to

itself. You must understand that all these definitions are to a certain extent ideal. There is no perfect solid, nor any perfect liquid, nor any perfect gas. The ideal states are not realized in nature; but as most bodies approximate more or less closely to one of the three states I have described, we are forced to conclude that there are *three principal molecular conditions* in which bodies can exist. We are far from understanding these conditions perfectly, but I shall try to give you a general idea of them, so far as we do understand them.

Molecular Constitution of Solids.—We are to consider that in solids the molecules have become relatively fixed, in some way as yet very imperfectly understood. I do not mean that they are motionless, however. They may be, and almost certainly are, in very active motion; but the point is, they do not *roam about* among one another. Each molecule executes a sort of vibration or oscillation about a mean or average position, from which mean position it does not of itself permanently depart; nor does it depart permanently from this mean position under the influence of small, temporary external forces. There is a stable equilibrium of some kind established, though I cannot tell you much more about it. You must not imagine that the vibration of a molecule in a solid consists in a simple periodic to-and-fro motion. The oscillations are probably of an exceedingly complicated nature. The parts of the molecule may be vibrating among themselves, and the molecule is almost certainly vibrating as a whole, in such a way that its center of gravity describes a tortuous curve, while the molecule executes a series of complex rotations.

Molecular Constitution of Liquids.—In liquids, the molecules no longer have determinate mean positions. They are in active motion, however, and in both solids and liquids they exert a powerful attraction on their neighbors. We are to conceive the molecules of a liquid as crowded closely together,

and continually curving about under the varying influence of their mutual attractions, each molecule winding its tortuous way in and out among the others perpetually. You will see that according to this conception any given molecule in a liquid may pass through every part of the liquid in the course of time, though its path is so crooked, and so continually bending back upon itself, that the molecule has to travel an enormous actual distance before it has departed very far from its starting point. I have made a purely imaginary sketch to

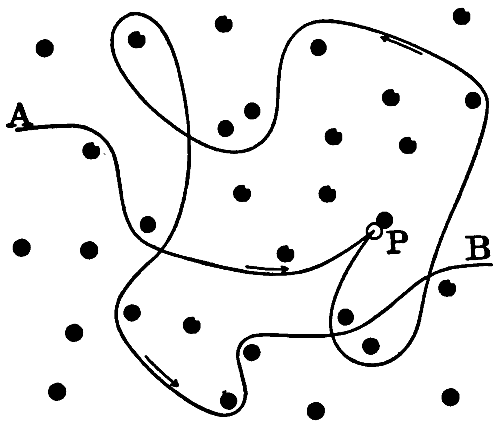


FIG. 10.—ILLUSTRATING MOLECULAR MOTION IN A LIQUID.

illustrate this kind of motion (Fig. 10). It represents a number of molecules, which, for the time being, we will suppose to be fixed. A molecule is supposed to enter this congregation at *A*, and the curve represents its motion until it leaves the system again at *B*. I have represented a *collision* with the molecule *P*, the moving molecule rebounding again and continuing its course. This sketch does not purport to represent the actual path described by a liquid molecule, and I present it to you only for the purpose of assisting your imagination a little. In the actual liquid all the molecules are moving, and a diagram of their true motions

would probably be so complicated that it would be quite unintelligible, even if we could construct it — which unfortunately we cannot. I may say, however, that collisions between liquid molecules are probably very much more frequent than the diagram indicates, and that the actual motions of the molecules of liquids are probably fully as complicated as they are in solids.

Molecular Constitution of Gases. — We are to conceive the molecules of a *gas* as possessing, on the whole, a higher velocity than those of liquids and solids. At least we have reason to believe that the molecules of any one gas have a higher velocity than these same molecules would have if the gas that they compose were liquefied or solidified by suitable means. Moreover, the molecules of gases are much further apart, on the whole, than the molecules of liquids and solids are. In fact it has been said, by way of popular illustration, that the molecules of gases are as far apart, in proportion to their size, as the fixed stars are. This is certainly not true. They are far enough apart, however, to be out of the range of one another's attraction during the greater part of the time; or, at least, out of the range of any *sensible* attractive influence. Now a body left to itself, and not acted upon by external forces, describes a straight line with unvarying velocity; and hence, you will see, we must conclude that the molecules of gases describe paths that are *sensibly straight.* This is a very important conclusion, and it underlies almost all of the reasoning about gases that I shall present to you this evening.

II. THE KINETIC THEORY OF GASES.

Preliminary Remarks. — The properties of gases are so remarkable, and the laws to which they are subject are so simple, that physicists were naturally led to believe that the easiest way to learn something about molecules would be, to

study the gaseous state of matter first. A great deal of thought has therefore been expended upon gases, and we now have some fairly accurate information about their molecular constitution. The phenomena of liquids and solids are so much more complicated, and so imperfectly understood, that it will probably be many years before our knowledge of the molecular structure of these bodies is at all comparable with our present knowledge concerning gases. For this reason I shall have to devote a considerable part of the evening to the discussion of gases, and comparatively little of it to liquids and solids.

Molecular Collisions, and Free Path.—When a multitude of bodies are moving about in the same region, in every conceivable direction and with every imaginable velocity, it is perfectly certain that there will be frequent *collisions* among them; and if we are to consider gases as aggregates of swiftly moving molecules, we shall have to introduce the idea of molecular collisions. The best popular description of a gas, according to the received kinetic theory, that I have heard, likens it to a wash-boiler full of furious bumble-bees, the bees corresponding to the molecules. The analogy is not perfect, however, and we must not press it too far. The molecules of a gas, as I have said, are believed to fly about in straight lines, in every conceivable direction. When two molecules collide, they bound apart like rubber balls, except that they are much more perfectly *elastic* than rubber balls. They crash into one another incessantly and fly apart again, only to crash into others and rebound as before. The space described by a molecule between two successive collisions is called its *free path;* and I may state a fact to which I have already called your attention, in the following more exact language: In the gaseous condition, the average free path of the molecules is so great, in proportion to the range of their power of sensible attraction, that during the greater part of the time, each molecule is practically uninfluenced by its

neighbors. You will observe that we do not say that a molecule has a *smaller attractive power* in the gaseous condition than it has in the solid or liquid condition. Such a statement as that would be indefensible. But if, at any instant, we could suddenly arrest all the molecules of a gas, and fix them just as they were at that instant, so that we could examine them at our leisure, we should find that the great majority of

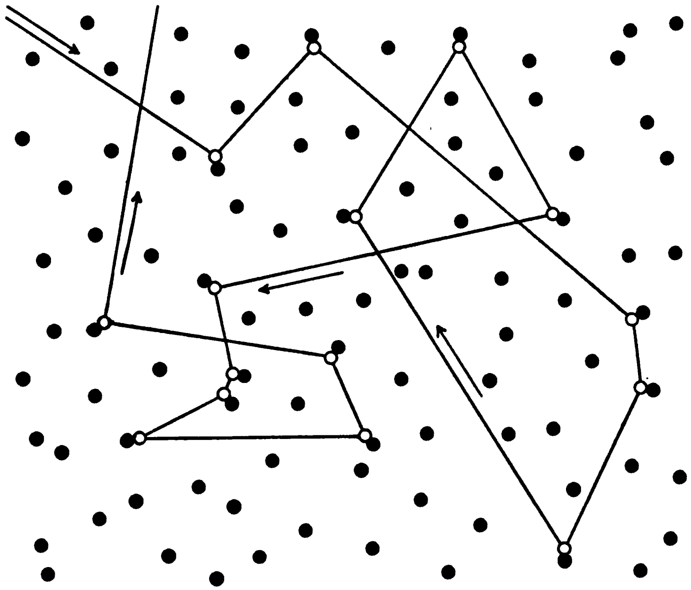


FIG. 11.—ILLUSTRATING MOLECULAR MOTION IN A GAS.

them were too far apart to exert sensible attractive powers on one another. The diagram (Fig. 11) may assist you to form a proper conception of the motion of a gaseous molecule. It represents the kind of path one molecule might describe in passing through an aggregation of other *fixed* molecules; but you must be careful not to infer anything about the shapes of the molecules, nor about their sizes as compared with their average distance from one another, either from this diagram

or from the corresponding one (Fig. 10) already given to illustrate the molecular motion in liquids.

The Cause of Gaseous Pressure. — If our conception of a gas is correct, it is plain that those molecules which are in the outer parts of a given mass of gas must beat incessantly upon the walls of the containing vessel, flying back again from these walls in the same way that they fly away from one another after collisions among themselves. This being the case, it is plain that the walls of the containing vessel are in the same condition as a *target* against which a perfect storm of bullets is striking perpetually. Such a storm of bullets would tend to force the target in the direction in which the bullets were moving before collision; and if the impacts were frequent enough, they would have an effect upon the target which could not be distinguished from a *continuous pressure.* And if we pass, in thought, from bullets to molecules, and from target to retaining vessel, we shall have a very good notion of the cause of gaseous pressure, as it is understood to-day.

Molecules are Perfectly Elastic. — If gaseous pressure is really due to molecular bombardment, there is one property of molecules that we can point out immediately. It is, that they are *perfectly elastic.* I am not sure how far the gentlemen present have followed the study of mechanics and physics, so at the risk of telling you something you could much better tell *me* all about, I am going to explain what I mean by the expression "perfectly elastic." If we drop a lead ball on the floor, it does not rebound at all; and we express this fact by saying that it is not elastic — or by saying that its elasticity is practically zero. If we drop a rubber ball on an unyielding surface, it does rebound, but not to the height from which we dropped it. We express this fact by saying that it is elastic, but not *perfectly* so. The rubber or glass or lead ball, in its original elevated position, possesses

a certain amount of potential energy, or energy of position. As it falls it loses this potential energy exactly in proportion to its approach to the floor; and as energy cannot be destroyed, the ball moves quicker and quicker, so that its kinetic energy increases just as fast as its potential energy decreases. When it reaches the floor it can go no further; but it has by that time acquired considerable velocity, and, consequently, considerable momentum; and the upper parts of the ball are crowded downward by their momentum, in spite of the fact that the lower part of the ball has come to rest. The obvious result is, that the ball is flattened out, something like this

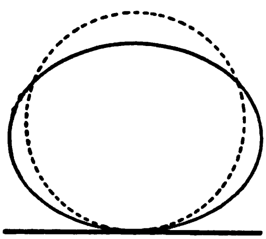


FIG. 12.—ELASTIC BALL STRIKING A HARD SURFACE.

(Fig. 12), where the dotted line shows the contour of the ball at the moment of striking the floor, and the full line shows the contour at the moment of maximum compression. The ball is now stationary, and its kinetic energy has entirely disappeared. What has become of it? Well, if the ball has *no elasticity at all*, its kinetic energy has all been transformed into energy of other kinds—principally into heat. On the other hand, if the ball is *perfectly elastic*, its kinetic energy has all been stored up in the ball as *internal potential energy;** and in another instant it will begin to be given out again as kinetic energy of translation, and the ball will go up in the air once more until it reaches the exact height from which it fell—unless the shock of the collision with the floor has set up *vibrations* in the ball, in which case it will not rise to the original height, but will fall short of it by an amount exactly corresponding to the amount of its internal energy of vibration. Now if molecules did not possess this property of perfect elasticity, then every time they collided with one another, or with the walls of the containing vessel, a portion

* The floor is here supposed to be perfectly rigid and unyielding, so that it does not absorb any of the energy of the ball.

of their kinetic energy would be dissipated as energy of some other kind; and hence in the course of time their velocities would grow materially less. For instance, if we had a mass of gas in a sealed bottle through which nothing was allowed to pass in either direction — not even light nor heat — in the course of time the molecules would come to rest, so far as any motion of translation is concerned, and in the place of a gas we should have a vacuum with a layer of inert molecules on the bottom of the bottle. (Of course there would still be in the bottle an amount of energy equal to the primitive kinetic energy of translation, rotation, and internal vibration of the molecules; but what form this energy would have, I cannot say.) This would imply that the gas had ceased to exist *as* a gas; and since we have no experimental evidence of such a phenomenon, it is plain that our hypothesis concerning the nature of gaseous pressure obliges us to admit the perfect elasticity of molecules. This is the first general property of molecules that we have arrived at; and in all that follows, this evening, I will ask you to bear it in mind. I ought to say a word, before passing on, about the possibility of the transformation of kinetic energy of translation into internal vibrational energy. This was hinted at, a moment ago, in discussing the behavior of the perfectly elastic ball. It has been maintained by numerous eminent physicists and mathematicians, that even if the molecules *were* perfectly elastic, their kinetic energy of translation and rotation would gradually be transformed into vibrational energy, so that the pressure of such a molecular medium as we have imagined would continually grow less, unless more energy were supplied from without. This was considered to be a grave objection to the kinetic theory of gases. From a mathematical analysis of the question, however, it appears that such a gradual increase in vibrational energy could not occur. I will not discuss this matter further, now, but will merely quote to you the present opinion of Lord Kelvin, who formerly believed that the vibrational energy of a system of mole-

cules must increase indefinitely, at the expense of the energy of translation and rotation. "I now see," he says, "that the average tendency of collisions between elastic, vibrating solids must be to diminish the vibrational energy, provided the total energy per individual solid is less than a limit depending on the shape or shapes of the solids: and hence, as nothing is lost of the whole energy, conversion of all but an infinitesimal proportion into translational and rotational energy must be the ultimate result."* Thus you will perceive, vibrational energy is practically eliminated from the problem, and we are justified in omitting it from consideration, for the present. This amounts to saying, not only that molecules are perfectly elastic, but also that the mean *coefficient of restitution* of a molecule is *unity*.

Velocities of Molecules Unequal. — Another fact that forces itself upon our attention is, that whatever the velocities of the molecules in a gas may be, they cannot be all alike. For if they were alike at any given instant, it is apparent that the frequent collisions among them would speedily destroy the equality, and we should shortly find some of them moving very rapidly, and others almost motionless. We shall see, later, that the number of collisions among the molecules of a finite portion of gas in a finite time, at ordinary pressures and temperatures, is prodigious; and we should meet with absolutely insuperable mathematical difficulties if we should attempt to trace the path of any one molecule in its zig-zag course among the others, with the idea of determining its individual velocity at any given moment. In fact, when we come to consider the actual number of molecules in gases under ordinary conditions, and the number of collisions that occur in any given time, I think we shall almost be ready to say that it would take the whole population of the sidereal universe millions of centuries to find out definitely what would happen in a single cubic inch of gas in one second.

* *Popular Lectures and Addresses*, Vol. I, p. 464.

Statistical Method of Investigation. — It would never do, however, to advance a theory and expect men to accept it, if it were so complicated as to defy mathematical investigation. A method of dealing with this problem has therefore been devised, which we may call the *statistical method.* We give up, at the outset, all idea of following the molecules individually, and regard gases as vast aggregates of moving particles, of which aggregates certain things of a statistical nature must be true. The whole kinetic theory of gases therefore becomes a sort of department of the theory of probabilities. Before passing to the consideration of the general facts that have been ascertained concerning great congregations of molecules, I want to say a word about this statistical method, which is really very beautiful, from a mathematician's point of view. The very fact that there *is* a statistical constancy in things is to me a continual source of wonder. For example, consider the number of persons that leave Worcester on any particular daily train — let us say, on the 10:13 train for New York. You will find that this train does not carry the same set of passengers on any two days, and yet the travel on it is fairly uniform in amount except when there is a foot-ball game in Springfield, or a Christmas dinner in prospect somewhere else, or some other pronounced and recognizable cause of disturbance. There are variations, of course, but they are not marked. Now why is it that this train is not empty on some days, and why do not all these people happen to want to go at once on some other days? If you can give a good answer to this seemingly stupid question, you will have made an excellent beginning in the kind of reasoning on which the kinetic theory of gases is based. The general principles on which this theory is founded are the same as those underlying *every* kind of statistical investigation; and you will find that the mathematical formulæ involved in all such investigations are of the same general form.

Fundamental Assumptions of the Original Kinetic Theory. — In the earlier mathematical investigations of the properties of gases, the molecules were assumed to be exceedingly small — almost mere points; and they were assumed to be almost infinite in number. They were, moreover, considered to be hard, smooth, spherical, and perfectly elastic, and to exert no influence on one another, when not in actual contact. These

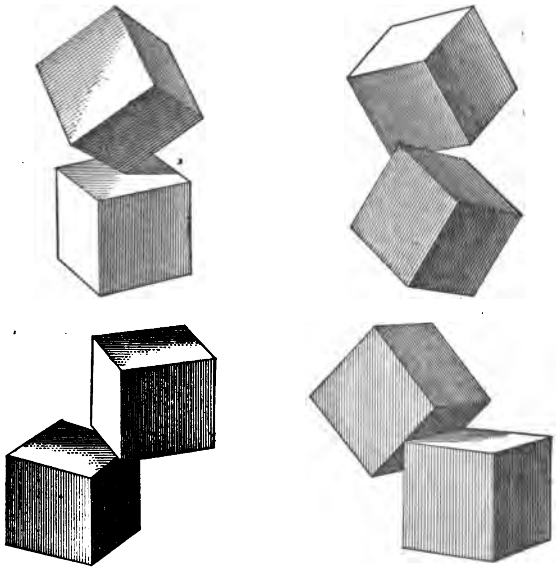


FIG. 13. — CUBES IN COLLISION IN VARIOUS WAYS.

properties (except the elasticity) were assumed, not because it was considered in the least probable that molecules have such properties, but in order to lessen the mathematical difficulties involved in the subsequent analysis; for these difficulties are great enough to satisfy anybody, even when the problem is made as simple as possible. It was proposed to make very simple assumptions, and then to trace out the results that would follow from them, and see how far these

correspond with the actual facts. This would give some idea of the admissibility, or inadmissibility, of the premises. I will try to explain the reasons for making the various assumptions I have mentioned. The molecules were assumed to be spherical, because spheres can collide with one another in only one way; whereas other bodies can collide in an infinite number of ways, as you will see by considering the case of a pair of cubes (Fig. 13). They were assumed to be hard, in order that collisions might be considered as having no sensible duration, and in order that we might not have to consider vibrations in the body of the molecule. They were assumed to be small, in proportion to the space in which they move, in order that the probability of a collision in which three or more molecules should come together at once might become vanishingly small in comparison with the probability of a collision in which the molecules come together in pairs; thus enabling us to avoid the discussion of the more complex collisions. They were assumed to be practically infinite in number, because statistical conclusions are not exact when only a small number of things are considered. They were assumed to be devoid of the power of attraction or repulsion, because the introduction of forces of this kind would greatly complicate the treatment of the problem; and moreover we have good experimental reasons for believing that in actual gases the effects of intermolecular attraction are slight. Finally, they were assumed to be smooth, in order that we might not have to take account of the rotations that would be established if rough spheres should collide. Those of you who play billiards may understand this better if I say that the molecules are supposed to be so smooth that they take no "english" from one another — the only force acting between them at the instant of collision being a radial force, as shown in the diagram (Fig. 14).

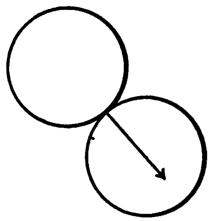


FIG. 14. — SMOOTH SPHERES IN COLLISION.

Maxwell's Theorem. — These premises being admitted, it may be proved that if the spheres, or ideal molecules, are once set in motion with equal velocities, or with *any distribution of velocities whatever,* their mutual collisions will very quickly bring them into such a state that the number of spheres having velocities between v and $v + dv$ will be

$$dN = \frac{4N}{a^3\sqrt{\pi}} \cdot \epsilon^{-\frac{v^2}{a^2}} \cdot v^2\, dv \tag{1}$$

In this expression N is the total number of the spheres, $\pi = 3.14159....$, $\epsilon = 2.71828....$ (the base of Napierian logarithms), and a is a constant quantity, whose value cannot be found unless we know some further circumstance about the motion of the spheres. If we know their average velocity, for example, we may determine a in the following way: There are dN spheres that have the velocity v; and hence the sum of the velocities of these dN spheres is $v \cdot dN$, and the sum of the velocities of *all* the spheres is

$$\sum (velocities) = \int_{v=0}^{v=\infty} v \cdot dN$$

Substituting in this expression the value of dN as given by equation (1), we have

$$\sum (velocities) = \frac{4N}{a^3\sqrt{\pi}} \cdot \int_0^\infty \epsilon^{-\frac{v^2}{a^2}} \cdot v^3\, dv$$

Upon effecting the integration this gives us

$$\sum (velocities) = \frac{4N}{a^3\sqrt{\pi}} \cdot \frac{a^4}{2} = \frac{2Na}{\sqrt{\pi}}$$

And since the average velocity (which we will represent by V_0) is one Nth of the sum of all the velocities, we have, upon dividing this last expression by N,

$$\left.\begin{aligned} V_0 &= \frac{2a}{\sqrt{\pi}} \\ \text{or} \qquad a &= \frac{V_0\sqrt{\pi}}{2} \end{aligned}\right\} \tag{2}$$

Let us next suppose that we know the total kinetic energy of the spheres, instead of their average velocity; and let it be required to find the value of a in terms of this energy. The kinetic energy of a sphere having the mass m and the velocity v, would be $\frac{1}{2}mv^2$; and there being dN spheres that have the velocity v, the sum of the kinetic energies of these dN spheres will be $\frac{1}{2}mv^2 . dN$, and the total kinetic energy of all the spheres will be

$$k = \int_{v=0}^{v=\infty} \tfrac{1}{2} mv^2 . dN \tag{3}$$

Substituting the value of dN from equation (1), we have

$$k = \frac{2\,Nm}{a^3\sqrt{\pi}} . \int_0^\infty \epsilon^{-\frac{v^2}{a^2}} . v^4 dv$$

Effecting the integration,* we have

$$\left.\begin{aligned} k &= \frac{2\,Nm}{a^3\sqrt{\pi}} . \frac{3\,a^5\sqrt{\pi}}{8} = \frac{3}{4}\,Nma^2 = \frac{3\,Ma^2}{4} \\ \text{or} \qquad a &= 2\sqrt{\frac{k}{3\,M}} \end{aligned}\right\} \tag{4}$$

where M is the total mass of the spheres. There is one equation which I should like to prove to you while we are discussing molecular velocities, because we shall have occasion to make use of it later on. If we represent the average of the squares of the individual velocities of the spheres by u^2, we have

$$u^2 = \frac{v_1^2 + v_2^2 + \dots}{N} \tag{5}$$

The total kinetic energy of the spheres is

$$k = \frac{mv_1^2}{2} + \frac{mv_2^2}{2} + \dots = \frac{m}{2}(v_1^2 + v_2^2 + \dots)$$

and we may substitute in this expression the value of $(v_1^2 + v_2^2 + \dots)$ as obtained from (5). We find that

$$k = \frac{Nmu^2}{2} = \frac{Mu^2}{2}$$

* The process of integration is given in the Appendix.

Substituting this value of k in the expression for a as given in equation (4), we have

$$a = \frac{2u}{\sqrt{6}}$$

Going back to equation (2), let us replace a in that equation by the value we have just found for it. We then have

$$V_0 = \frac{4u}{\sqrt{6\pi}} = .9213\,u \qquad (6)$$

This equation is important, because it enables us to calculate the *average velocity*, V_0, when the "mean-square" velocity, u, is given.

Illustrations of Maxwell's Theorem. — If equation (1) be integrated between the limits $v = 0$ and $v = mV_0$, we shall obtain the number of spheres whose velocities, at any given instant, lie between 0 and mV_0. The integral in question is a famous one, and, being what mathematicians call a "gamma function," it is not expressible in terms of any other functions with which you are likely to be familiar. Let me pass over the process of integration, therefore, and give you only the results contained in this table.* The first and third columns give the different values of m for which I have computed the

Table of the Number of Spheres having a Velocity of mV_0 or less.

m	Spheres Having Velocity mV_0 or Less.	m	Spheres Having Velocity mV_0 or Less.
$\frac{1}{4}$	.0161	1	.5330
$\frac{1}{3}$	.0368	2	.9829
$\frac{1}{2}$	.1120	3	.999958
$\frac{2}{3}$	.2306	4	.9999999926
$\frac{3}{4}$	.3020		

* The process of integration is given in the Appendix.

integral, and the second and fourth columns give the number of spheres that have, at any given instant, a velocity of $m V_0$ or less. (The "number of spheres" is expressed as a decimal fraction of the *whole number in the medium.*) You will notice that only 1.61 per cent of the spheres will have velocities as small as one-fourth of the average velocity, and that over 98 per cent of them will have velocities less than *twice* the average velocity. The range of the velocities of the spheres will therefore be comparatively small; and only a surprisingly small proportion of them will have velocities that could properly be called great, in comparison with the average velocity of all. Less than one in a hundred million will be moving as fast as four times the average speed; and I could show you that less than one sphere in 10^{53} will be moving as fast as ten times the average speed. I have plotted for you (Fig. 15) the curve whose equation is

$$y = \frac{4}{\sqrt{\pi}} \cdot \epsilon^{-\left(\frac{v}{a}\right)^2} \cdot \left(\frac{v}{a}\right)^2 \qquad (7)$$

and the plot may serve to give you a better idea of the actual distribution of the velocities of the spheres than you could get from a study of the integral itself. The abscissæ represent velocities, and the ordinate, for any abscissa v, is propor-

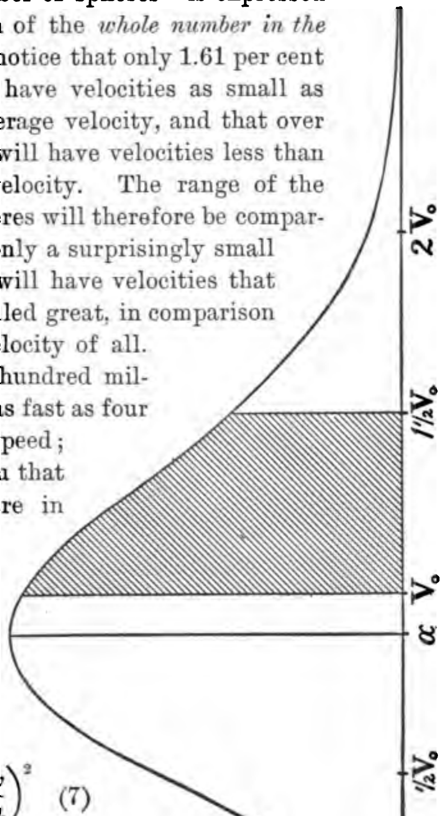


FIG. 15.—ILLUSTRATING THE DISTRIBUTION OF MOLECULAR VELOCITIES IN A GAS.

tional to the number of spheres having a velocity between v and $v + dv$. I have marked the ordinate corresponding to the average velocity, V_0, and those corresponding to $\frac{1}{2} V_0$, $1\frac{1}{2} V_0$, and $2 V_0$. I have also marked the ordinate corresponding to the quantity a which occurs in equations (1) and (7), and you will see that it is the greatest ordinate of the curve. The area included between any two ordinates represents the number of molecules whose velocities lie between the values of v that correspond to those ordinates. Thus the shaded area represents the number of molecules whose velocities, at any given instant, lie between V_0 and $1\frac{1}{2} V_0$. If one ordinate were drawn at the origin and the other at infinity, the area between them (which would then be the entire area of the curve) would represent the number of molecules whose velocities, at any given instant, lie between 0 and ∞. In other words, the area of the entire curve represents the whole number of molecules present in the gas under consideration. If we should measure the area of the shaded part with a planimeter, and divide the result by the area of the whole curve, the quotient would represent the number of molecules whose velocities lie between V_0 and $1\frac{1}{2} V_0$, *expressed as a fraction of the whole number of molecules present.* By proceeding in this way we could construct a table similar to the one I have just given you, without resorting to the somewhat laborious process of integrating equation (1). You will note that the curve approaches the axis of v indefinitely, but that it does not actually touch it except at infinity. It follows that it is *possible* for a given sphere to have any velocity whatever; but the *probability* of the higher velocities is vanishingly small. In fact I have told you that there is only one chance in 10^{53} of a given sphere having a velocity as great as ten times the average velocity; and the probability of higher velocities is still smaller, until the probability of an infinite velocity becomes zero.

Determination of the Average Velocity of Translation of Hydrogen Molecules. — It may interest you to see how the average velocity of translation of the molecules of a gas may be determined. For this purpose we shall assume for the moment that gases are really composed of spherical molecules such as I have described to you. In that case all the energy the gas possesses must be kinetic energy of translation; for we have assumed that there are no intermolecular forces, and no internal vibrations; and we have also assumed that the collisions do not give rise to rotations. We shall not take air for our example, because air is a mixture of different kinds of molecules; and we have not yet considered the properties of mixtures. Let us therefore take hydrogen. At a pressure of 14.7 pounds per square inch (or say 2117 pounds per square foot), and at the temperature of melting ice, a cubic foot of hydrogen weighs .005592 of a pound. Imagine this quantity of hydrogen enclosed in a cylinder (Fig. 16) having precisely one square foot of cross-sectional area, and an infinite length; and conceive it to expand indefinitely, pushing the piston P before it, the resistance of the piston being so regulated as to just allow the gas to expand. Then if x is the distance of the piston from the cylinder head at any moment, and p is the pressure exerted by the hydrogen on the entire piston at that moment, the work done by the gas in pushing the piston a distance dx is $p.dx$; and the work done in pushing it from $x=1$ (the starting point) to $x=\infty$ is

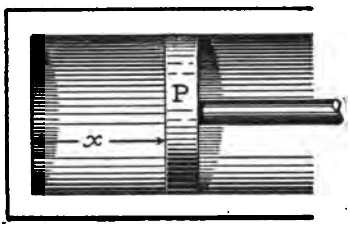


FIG. 16. — ILLUSTRATING ADIABATIC EXPANSION.

$$Work = \int_{x=1}^{x=\infty} p \,.\, dx. \tag{8}$$

Now if we want to find out how much energy is in the gas,

we must not let it either receive or give up heat; and you will find, when you study thermodynamics, that this condition is expressed by the equation

$$px^{1.41} = C \tag{9}$$

where C is a constant. To determine C, let us observe that we know that when $x = 1$, $p = 2117$; so that the value of C, in this case, is 2117, and the adiabatic equation becomes

$$px^{1.41} = 2117, \quad \text{or}$$
$$p = \frac{2117}{x^{1.41}}.$$

Substituting this value of p in (8), we have

$$Work = 2117 \int_1^\infty \frac{dx}{x^{1.41}} = 5163 \text{ foot pounds.}$$

Now on the assumptions we have made, this must be equal to the united kinetic energy of the molecules; or to

$$\tfrac{1}{2} m (v_1^2 + v_2^2 + \ldots) = \frac{Nm}{2} \cdot \frac{(v_1^2 + v_2^2 + \ldots)}{N} = \frac{M}{2} \cdot u^2$$

where u^2 is the quantity defined by equation (5), and M is the total mass of the gas. Hence we have

$$\tfrac{1}{2} Mu^2 = 5163. \tag{10}$$

Now the weight of the hydrogen under consideration being .005592 of a pound, its mass will be $.005592 \div 32.2 = .0001737$. Substituting this for M in equation (10), and solving for u, we have

$$u = 7710, \text{ and } V_0{}^* = 7103 \text{ feet per second.}$$

You will please notice that it is not claimed that this *is* the average velocity of hydrogen molecules. All that can be said of it is, that it is their average velocity provided the assumptions about them that I described to you a few moments ago

* See equation (6).

correspond to the actual facts. I shall shortly give you a better determination of the velocity of the molecules of a gas — one which is independent of the assumption of any particular form for the molecules.

Properties of Gaseous Mixtures. — If the kind of reasoning by which equation (1) was obtained is applied to a medium composed of a set of N_1 spheres each with the mass m_1, a set of N_2 spheres each with the mass m_2, and so on, the spheres in each set being exactly alike and very numerous, and every sphere being hard, smooth, small, and perfectly elastic, as before, we shall find that the different sets will mix with one another uniformly, and that the velocities in the spheres of each set will be distributed precisely as though the other sets were not present. The most familiar example of a gaseous mixture, in nature, is air; and one of the most striking things about air is its constancy of composition. In a chemical compound we should expect the proportions of the components to be constant; but in a mere mechanical mixture of oxygen and nitrogen, for instance, we might naturally expect to find a material difference in composition in two samples, when one is taken, say, on the Himalaya Mountains, and the other on the shores of the Arctic Ocean. The fact that no such difference in composition exists becomes particularly significant when we know that the kinetic theory shows that constancy of composition would necessarily result, if gases really are composed of small spherical molecules such as I have described. Another very important deduction, due, I believe, to Maxwell, is that in a mixture composed of several sets of elastic spheres, the average velocities in the different sets will not be equal; the set in which the molecules are heaviest will have the smallest average velocity; and, in general, the velocities will be such that the average kinetic energy of a molecule of one set will be precisely equal to the average kinetic energy of a molecule of any other set. This is one of the most remarkable propositions in the whole kinetic theory of gases.

Degrees of Freedom. — I am going to tell you of some much more general theorems about gases, but before doing so I want to explain what is meant by the expression "degrees of freedom." A particle constrained to move in a given straight line is completely described when we have stated its distance from some fixed point in that line. A particle constrained to move in a given plane is completely described when we have stated its distance from two fixed, intersecting straight lines in that plane. A particle in space is completely described when we have stated its distance from three fixed, intersecting planes. In the first case we say that the particle has *one degree of freedom,* because it has only one coördinate; in the second case we say it has *two degrees of freedom,* because it has two coördinates, either one of which may vary independently of the other. In the third case we say that the particle has *three degrees of freedom,* because it has three coördinates, any one of which may vary, independently of the others. The *Century Dictionary* defines a degree of freedom as "an independent mode in which a body may be displaced." The number of degrees of freedom of a body in free space can never be less than three. It may be more than three, however. In fact, it must be more than three, if the body is anything more than a mere particle. Consider, for example, a finite straight line, of given length. One end of it, say A, has three degrees of freedom — it can be anywhere in space. The other end, B, also has three *coördinates,* but between these coördinates and those of A there is an equation expressing the fact that the length of AB is constant. By means of this equation we could eliminate one of the six coördinates, leaving only five that are really *inde-*

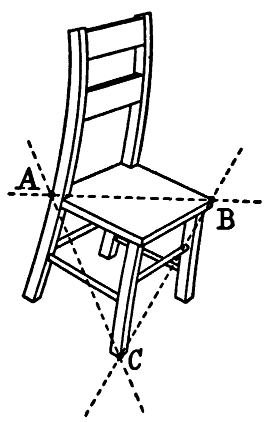


FIG. 17. — A RIGID BODY IN SPACE.

pendent; and we therefore say that such a line as this has five degrees of freedom. A rigid body in space has *six* degrees of freedom: it becomes fixed when three of its points are given. Consider, for instance, the points A, B, and C, in this sketch (Fig. 17). Each of these points has three coördinates, making nine coördinates in all; and among these there are three equations, expressing the constancy of the distances AB, BC, and CA. By means of these three equations we can eliminate three of the nine coördinates, leaving only six that are really independent; and hence we say that rigid bodies have six degrees of freedom. Bodies that are not rigid have more than six degrees of freedom; the number of degrees that they possess being always determined by the number of independent coördinates required to fix them. For example, a series of n jointed rods has $(2n+3)$ degrees of freedom. We may perhaps get a clearer idea of the precise significance of the expression "degrees of freedom" by selecting a *mixed* system of coördinates for defining the position of a body. Let us, for example, again consider a rigid body in space. The center of gravity of this body is free to move parallel to any of the three axes of reference. (This is the same thing as saying that the center of gravity of the body is perfectly free, because any imaginable motion of it can be resolved into components parallel to x, y, and z. See Fig. 19.) Moreover, the body is free to rotate about three axes, parallel respectively to x, y, and z. (All other rotations can be resolved into component rotations about these three axes. See Fig. 20.) Considering the three translations and the three rotations, we see that a rigid body in space has six degrees of freedom. Similarly, a geometrical figure constrained to move in a plane has three degrees of freedom: its center of gravity can move parallel to either axis, and

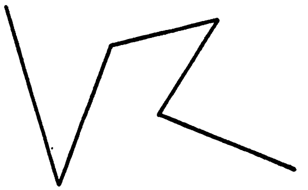


FIG. 18.—A SYSTEM OF JOINTED RODS.

the figure itself can rotate about an axis perpendicular to the plane in which it is constrained to move. If I have made the meaning of the expression "degrees of freedom"

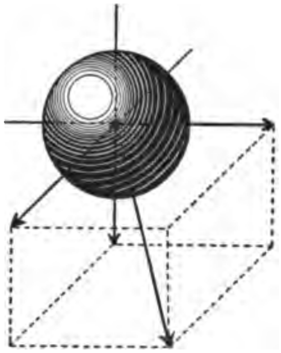


FIG. 19.—A SPHERE WITH THREE COMPONENT TRANSLATIONS.

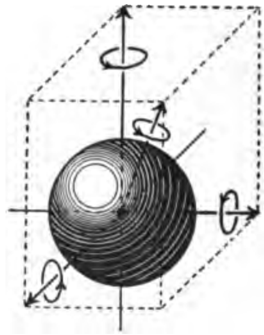


FIG. 20.—A SPHERE WITH THREE COMPONENT ROTATIONS.

clear to you, we are prepared to pass to the consideration of the more general theorems about molecules that I spoke of a moment ago.

Generalized Theorems.—In the earlier days of the kinetic theory of gases, molecules were assumed to be spherical, in order to avoid the tremendous mathematical difficulties that would arise if any other form were assumed. There are excellent reasons, however, for believing that most molecules are not spherical; and mathematicians therefore turned their attention to the more general case in which *no* particular shape was assumed. You will understand that the analysis of this general problem is very difficult; but a satisfactory amount of progress has been made with it, and I will tell you what has been discovered, thus far. Let us consider a medium composed of any number of sets of bodies, such that the bodies belonging to each set are exactly like one another, though a body belonging to *one* set may be totally unlike a body belonging to *another* set. Let these bodies have any

number of degrees of freedom (which number of degrees may be different in the different sets), and let them be acted on by parallel forces (such as gravity), or by forces tending towards fixed centers, or by internal forces (that is, forces acting within the individual bodies, between their parts). Let all the bodies be very small in comparison with the total space they occupy, so that the chance of their colliding three or more at a time is practically nothing. Moreover, let them be very numerous, and let them be perfectly elastic, and let them be smooth, so that when they collide the only force tending to make them rotate is that due to normal impact. Let them be set in motion among one another with any distribution of velocities; and let them be hard, but not infinitely so, the force called into play during collision being very great, but not necessarily infinite (as it would be if the hardness were infinite); and let the duration of a collision be exceedingly short, yet not necessarily zero. These are the assumptions made by the kinetic theory of gases as it exists to-day. You will see that they are vastly more general than those I described to you in connection with the earlier investigations. The conclusions that have been drawn from them are as follows: (1) After a short time, the law of distribution of positions and velocities in each set of the generalized bodies (or molecules, as we shall call them henceforth) will be precisely the same as it would be if all the other sets were absent; so that each set behaves as a vacuum to all the rest, so far as the distribution of velocities, and the density of aggregation of the molecules in any given region, are concerned. (2) This law of distribution of the velocities in each set of molecules is the same as that given for spherical molecules in equation (1). (3) The average kinetic energy of translation of the molecules of any one set is equal to the average kinetic energy of translation of any other set. (4) *The total kinetic energy of each set of molecules is divided up equally among the different degrees of freedom of that set.* This last theorem is undoubtedly the most remarkable proposition

about molecules ever enunciated. It is due to Boltzmann, and it seems not to have met with unqualified acceptance among mathematicians. Lord Kelvin, even, says that he "never felt it possible to believe in that theorem regarding the distribution of energy." My opinion is worth little, compared with his, yet it seems to me that there can be no doubt about the validity of the reasoning on which this theorem is based, *provided* internal vibrations are excluded from consideration. It has never seemed proper, to me, to consider a possible mode of vibration as a "degree of freedom"; and I think that it is the extension of Boltzmann's theorem to the *vibrational energy* of molecules that gives rise to the objections of Lord Kelvin and others. The theorem does not apply to single molecules, of course. Any molecule, selected at random, may not be rotating at all, or it may be rotating about some axis and yet have its center of gravity stationary, or it may be entirely motionless, or it may have component motions of translation parallel to all three axes, and a rotation which is the resultant of rotations about three axes, parallel to x, y, and z, respectively; and if the molecule is not a rigid body, it may have other motions also — as many, in fact, as it has degrees of freedom. But Boltzmann's theorem asserts that if rectangular axes be drawn in a medium composed of a multitude of flying molecules, each with n degrees of freedom, the *total kinetic energy in the medium* will be so distributed that one nth of it will be due to the velocity-components that are parallel to x, one nth to the velocity-components that are parallel to y, one nth to those that are parallel to z, one nth to the rotation-components whose axes are parallel to x, one nth to the rotation-components that are parallel to y, and so on, one nth of the total kinetic energy of the medium being due to the sum of the component motions in each degree of freedom. I think you will see, now, why the determination of the average velocity of hydrogen molecules that we made a little while ago, is unsatisfactory. We considered only the kinetic energy due

to the *translation* of the molecules; and this amounted to assuming that the molecules are not set in *rotation* by their collisions. We shall see, later, that hydrogen molecules *are* set in rotation by their collisions; and we shall find, in consequence, that the average velocity we deduced for them was too great.

Adaptation of the Foregoing Equations to the Generalized Kinetic Theory. — The extension of our conception of molecules, from spheres to smooth, elastic bodies of any form, does not involve any very radical changes in the formulæ deduced from the consideration of the motion of the spheres. Thus equation (1) will still express the number of molecules whose velocities of translation lie between v and $v + dv$, and equations (2) will also hold true, since they are derived from (1) by a process of reasoning which in no way involves the form of the molecules. But we can no longer consider the kinetic energy of the molecules to be all *translational.* In fact, Boltzmann's theorem tells us that the kinetic energy is divided up equably among the different degrees of freedom; and as translation involves only *three* degrees of freedom, it follows that the kinetic energy of translation, in a gas, is equal to $\frac{3}{n} \cdot k$; where n is the total number of degrees of freedom possessed by a molecule of the gas, and k is the total kinetic energy in the gas. Hence, for k, in equation (3), we must write $\frac{3k}{n}$; and we must make the same substitution in (4), which is derived from (3). Therefore (4) becomes

$$\left.\begin{aligned} \frac{3k}{n} &= \frac{3Ma^2}{4} \quad \text{and} \quad a = 2\sqrt{\frac{3k}{n} \cdot \frac{1}{3M}} \\ \text{or} \qquad k &= \frac{nMa^2}{4} \quad \text{and} \quad a = 2\sqrt{\frac{k}{nM}} \end{aligned}\right\} \tag{11}$$

Equation (6) remains unchanged, since k does not appear in it.

Gaseous Pressure. — I am sure I have nearly exhausted your patience with mathematical formulæ; but there are one or two things more to which I want to call your attention, before passing on to matters involving less mathematics. By considering the molecules as projectiles striking against the walls of the containing vessel, we may find out what their mean velocity must be, in order to produce the observed pressure of the gas. The advantage of this method over the one I have already given you in discussing hydrogen gas is, that it does not require us to make any assumptions concerning the constitution of the molecules, except the very general one that their elasticity is perfect — or, more correctly speaking, that their average "coefficient of restitution" is unity. Without going through with the actual calculation (which would involve theorems in mechanics that you have probably not yet studied), let me say that if we confine our attention to one kind of gas — that is, to a gas whose molecules are all alike, each having n degrees of freedom — and if we assume that there are no forces except those due to collisions, then the expression for the pressure against a unit area of the containing vessel comes out

$$p = \frac{2\,k\Delta}{nM} \tag{12}$$

where Δ is the absolute density of the gas, M is its total mass, and k is its total kinetic energy. Now if the velocities of translation of the individual molecules are v_1, v_2, v_3, ..., and m is the mass of a single molecule, then the *kinetic energy of translation* of the system will be

$$\frac{m}{2}\left(v_1^2 + v_2^2 + v_3^2 + \ldots\right).$$

Substituting the value of the parenthesis as obtained from equation (5), the expression for the kinetic energy of translation becomes

$$\frac{1}{2}\,Nmu^2, \text{ or } \frac{1}{2}\,Mu^2,$$

since $M = Nm$. Translation involves only three degrees of freedom; and hence, by Boltzmann's theorem, we have the proportion

$$\frac{1}{2} Mu^2 : k = 3 : n$$

or

$$k = \frac{1}{6} nMu^2.$$

Substituting this value of k in (12), we have

$$p = \frac{u^2 \Delta}{3}. \tag{13}$$

From this equation we can calculate the value of u when we know the pressure and density of a gas; and having found u, we can calculate V_0 by means of equation (6).

Recalculation of the Average Molecular Velocity in Hydrogen. — A cubic foot of hydrogen at 32° Fahr. and under atmospheric pressure (*i.e.*, 2117 pounds to the square foot) weighs .005592 of a pound. Hence its mass is $\frac{.005592}{32.2}$, or .0001737. Substituting this for Δ and 2,117 for p, in (13), we have

$$u = \sqrt{\frac{3 \times 2{,}117}{.0001737}} = 6{,}047.$$

Then, from equation (6), we have

$$V_0 = 6{,}047 \times .9213 = 5{,}571 \text{ feet per second,}$$

which is the average velocity of hydrogen molecules, under the given conditions. If two gases have the same pressure, then, by (13),

$$u_1^2 \Delta_1 = u_2^2 \Delta_2$$

or

$$\frac{u_1}{u_2} = \sqrt{\frac{\Delta_2}{\Delta_1}}. \tag{14}$$

And as equation (6) shows that the average velocity of the molecules of a gas is proportional to u, it follows from (14) that in any two gases having the same pressure, the average

molecular velocities are inversely proportional to the square roots of the densities of the gases. This enables us to calculate the molecular velocities in other gases very readily, when the molecular velocity of any one gas is known. By the help of equation (14) and the velocity we have just obtained for hydrogen, I have calculated the following table of the average molecular velocities in several familiar gases.

TABLE OF THE AVERAGE MOLECULAR VELOCITIES OF GASES, IN FEET PER SECOND, AT 32° FAHR., AND ATMOSPHERIC PRESSURE.

GAS.	DENSITY. (H = 1)	AVERAGE VELOCITY.
Hydrogen	1.00	5,571
Oxygen	15.96	1,394
Nitrogen	14.01	1,488
Carbonic Oxide	13.96	1,491
Carbonic Acid	21.94	1,189

Pressure Produced by Several Sets of Molecules. — I have told you that the mathematical investigation of the generalized molecules described a few moments ago, shows that if there are several sets of such molecules flying about in the same field, the distribution of each set, and the distribution of velocities in each set, will be the same as though the other sets were not present. It follows from this that the pressure on the bounding walls, produced by all the sets together, will be equal to the sum of the pressures that the several sets would produce, if each existed in the same space alone. You will probably recognize this as the equivalent of Dalton's law, which states that in a mixture of gases the resulting pressure is the sum of the partial pressures due to the several constituent gases. Another way of stating this law is, In a mixture of gases, each behaves like a vacuum to all the rest

Avogadro's Law. — Going back to equation (12), let us confine our attention for the moment to a unit volume of gas. In this case M becomes identical with Δ; for, by definition, the absolute density of a gas *is its mass per unit volume.* Hence (12) becomes

$$p = \frac{2k}{n}. \qquad (15)$$

Now if two gases have the same pressure, that is, if $p_1 = p_2$, we have, from (15),

$$\frac{2k_1}{n_1} = \frac{2k_2}{n_2}.$$

From this equation it also follows that

$$\frac{3k_1}{n_1} = \frac{3k_2}{n_2}.$$

But we have seen that either member of this equation represents the *kinetic energy of translation* of the molecules of the corresponding gas. Hence it follows that if two gases have the same pressure, they will have, per unit of volume, the same kinetic energy of translation. Now if k' represents the kinetic energy of translation *per molecule,* and N is the number of molecules per unit volume, then we may express this last fact thus: If two gases have the same pressure, then

$$N_1 k'_1 = N_2 k'_2.$$

So that if $k'_1 = k'_2$, then $N_1 = N_2$. Hence, finally, we may say that if any two gases have the same pressure, and the same kinetic energy of translation *per molecule,* then these gases will contain the same number of molecules per unit volume. If we read "temperature" in the place of "kinetic energy of translation per molecule," this statement becomes identical with Avogadro's law.

Boyle's Law. — Returning once more to equation (12), let us observe that the definition of "density" gives us, in all cases, the equation

$$\Delta = \frac{M}{v}.$$

Substituting this value of Δ in (12), we have

$$p=\frac{2k}{nM}\cdot\frac{M}{v}, \text{ or } pv=\frac{2k}{n}. \tag{16}$$

We may, for convenience, transform this equation thus:

$$pv=\frac{2}{3}\cdot\frac{3k}{n}=\frac{2}{3}\cdot Nk' \tag{17}$$

where k' is the kinetic energy *of translation,* per molecule, and N (which does not vary so long as we confine our attention to some particular mass of gas) stands for the number of molecules in the gas under consideration. We are strongly reminded, by this equation, of Boyle's law, which states that the product, pv, is constant so long as the *temperature* of the gas does not vary; and if we make the single assumption that the sense-impression that we call "temperature" is really our mode of perceiving molecular *kinetic energy of translation,* we shall find that the results of the kinetic theory of gases correspond very closely with the facts as actually observed.

Results of the Kinetic Theory Compared with the Results of Observation. — These correspondences may be exhibited as follows:

Results of the Kinetic Theory.	Results of Observation.
1. When two or more sets of molecules are put into the same region of space, they diffuse into one another, until the molecules of each set become uniformly distributed throughout this space.	1. When two or more gases are put into the same vessel, they diffuse into one another, until each becomes uniformly distributed throughout the vessel.
2. The density of a medium composed of several sets of molecules is equal to the sum of the densities the individual sets would have, if each existed separately in a space equal to the given space.	2. The density of a gaseous mixture is equal to the sum of the densities of its component gases.

RESULTS OF THE KINETIC THEORY.	RESULTS OF OBSERVATION.
3. The pressure on the boundaries, due to a medium composed of several sets of molecules, is equal to the sum of the partial pressures due to its constituent sets.	3. The pressure on the containing-vessel, due to a gaseous mixture, is equal to the sum of the partial pressures due to the constituent gases (Dalton's law).
4. In a molecular mixture there is one physical quantity which is the same for every set of molecules; and that is, the average *kinetic energy of translation, per molecule.*	4. In a gaseous mixture there is one physical property which must be the same for each of the constituent gases; and that is, the *temperature.*
5. If two molecular aggregates exert the same pressure on their containing-walls, and have the same *kinetic energy of translation, per molecule,* then they will also contain the same number of molecules per unit of volume.	5. If two gases exert the same pressure on their containing-vessels, and have the same *temperature,* then they will also contain the same number of molecules per unit of volume (Avogadro's hypothesis).*
6. In any given mass of a molecular aggregate, the product of the pressure and volume is proportional to the average *kinetic energy of translation, per molecule.*	6. In any given mass of gas, the product of the pressure and volume is proportional to the *absolute temperature.* (This includes the laws of Boyle, Charles, and Gay Lussac.)

Temperature. — It is evident that there is a sufficient agreement between the properties of actual gases, and those of the ideal molecular medium we have considered, to make it very probable that gases have some such constitution as we have imagined the molecular medium to have. At all events we have found, as yet, no contradictions. You may not be ready to admit, however, that the assumption made

* I have included Avogadro's hypothesis among the "observed properties," because it was inferred from observation before it was deduced from a study of the motions of discrete elastic particles.

with regard to *temperature* is an admissible one. The discussion of this point belongs properly to thermodynamics, but since it has a close bearing on molecular theories, you may allow me to say a few words about it. We all know what is meant when we say that one body is hotter or colder than another — we refer to certain sensations that would be experienced if we should touch the bodies, or come very near to them; but it is quite a different thing to devise a rigid scale that will enable us to *measure* differences in temperature in such a way that we can say that a difference of 10°, for instance, on one part of the scale, is equivalent, in some sense, to a difference of 10° on any other part of it. In order to devise such a scale we shall have to fall back on some general principle or law; and our "temperature sense" does not furnish us any such principle — at least, not with any that is sufficiently exact for scientific purposes. It is necessary, therefore, to seek for some such principle in the world outside of ourselves, and to define "temperature" arbitrarily, so as to make it to conform to that principle; always remembering, of course, that the scale of temperature finally selected must be such, that measures obtained by means of it shall not be perceptibly inconsistent with the crude observations we can make directly, by means of our temperature sense. The commonest form of thermometer consists of a glass vessel containing mercury. It is graduated by immersing it in the steam arising from boiling water, and in a mixture of ice and water, marking the points at which the mercury stands under these circumstances, and dividing the space between these marks into (say) 100 equal parts, which are called degrees. The scale so formed is perfectly arbitrary, since it involves whatever peculiarities of expansion mercury may have; and these peculiarities cannot be investigated, without reasoning in a circle, unless we can find some kind of an absolute scale of temperatures which shall be independent of the properties of any particular substance. The mercury thermometer does not contradict our senses, it is true, but neither would ther-

mometers made with a host of other liquids; and yet the thermometers made with these other liquids would not agree among themselves, nor with the mercury thermometer. (Water is inadmissible as a thermometric fluid, for low temperatures at any rate, because near the freezing point it gives readings that contradict the direct evidence of the senses.) Now, I am not going to take you into the mazes of thermometry. I wanted to call your attention to the fact that "temperature" is not such a definite conception as one would be apt to imagine unless he had thought it over carefully, and that a thermometer scale is an arbitrary thing. I thought this might make it easier for you to admit that "temperature" may be the sense-impression that corresponds to molecular kinetic energy of translation. Yet I should not want to leave you with the impression that heat measurement is not an exact science. Let me add, therefore, to what I have said, that Lord Kelvin has provided us with what he calls an *absolute thermometric scale*, which is quite independent of the properties of any particular body. He obtains this scale from thermo-dynamical considerations,* and although his definition of temperature is quite as arbitrary as any other definition of it, it is the only one yet proposed that rests on a thoroughly scientific basis. For the purpose of fixing the size of his degrees, he defines the difference in temperature between boiling water and melting ice to be 100°; and he then finds that the temperature of melting ice, on his "absolute scale," is 273.1°. Furthermore, he finds that the readings of the air thermometer are almost identical with those of his absolute scale, provided allowance is made for the difference of 273.1 Centigrade degrees that exists between the zero of the absolute scale and the zero of the ordinary Centigrade scale. I have made out a table, here, giving the corrections to the readings of several kinds of thermometers, to reduce them to their equivalents on Lord Kelvin's absolute scale. In all but the last column the readings are supposed to have

* See the article *Heat*, in the *Encyclopædia Britannica*.

been previously corrected for calibration, expansion of the glass, error of the fixed points, etc., and the table gives only the correction that is made necessary by the imperfection of the thermometric fluid itself. The last column gives the corrections to be applied to a certain crown-glass, mercurial thermometer that was investigated by Regnault. The corrections in this column are far smaller than those in the preceding one, because they include the correction due to the expansion of the glass, and the glass-expansion and mercury-expansion corrections are of opposite sign.

TABLE OF CORRECTIONS, FOR REDUCING THERMOMETER READINGS TO THE ABSOLUTE SCALE.

READING OF THERMOMETER. (Centigrade Degrees.)	THERMOMETRIC SUBSTANCE.			
	AIR. (Constant Volume.)	AIR. (Constant Pressure.)	MERCURY. (Alone.)	MERCURY AND CROWN GLASS.
0°	0°.00	0°.00	0°.00	
20	− .03	− .04	+ 0 .20	
40	− .04	− .05	+ 0 .29	
60	− .04	− .05	+ 0 .30	
80	− .02	− .03	+ 0 .20	
100	.00	.00	0 .00	0°.00
120	+ .03	+ .03	− 0 .29	+ .08
140	+ .06	+ .07	− 0 .70	+ .21
160	+ .10	+ .11	− 1 .19	+ .36
180	+ .14	+ .16	− 1 .80	+ .51
200	+ .18	+ .20	− 2 .49	+ .48
220	+ .22	+ .25	− 3 .29	+ .42
240	+ .27	+ .29	− 4 .17	+ .37
260	+ .31	+ .34	− 5 .15	+ .11
280	+ .36	+ .39	− 6 .23	− .16
300	+ .41	+ .44	− 7 .39	− .67

Absolute Zero. — One of the most interesting things about the absolute scale is, that it has a zero — usually called the *absolute zero* — below which it appears to be impossible to

cool things. You will note the bearing of this on the kinetic theory of gases; for if temperature is really our mode of perceiving the translatory kinetic energy of molecules, then if we should gradually abstract from a gas its translatory kinetic energy, its temperature would seem to fall lower and lower, until finally, when we had abstracted all of this energy, the temperature would reach a point lower than which it could not go. There would no longer be any translatory kinetic energy to perceive; and hence we should have reached an absolute zero, below which it is not thinkable that the gas could be cooled. I may say, in fact, that if we define temperature as Lord Kelvin defines it (and this is the only rational way yet proposed), and if we admit that the sense-impression that we call "temperature" is our mode of perceiving the kinetic energy of translation of molecules, then the kinetic theory of gases becomes even more remarkable than we have found it to be; because we can then deduce from it all the fundamental equations of thermodynamics.

Ratio of the Specific Heats of Gases. — If a certain mass of gas, having a volume v_0 at the pressure p_0, expands adiabatically — that is, without either receiving or giving out heat *as* heat — we know from thermodynamics that its pressure and volume are connected by the relation

$$p_0 v_0^\gamma = p v^\gamma \tag{18}$$

where γ is the ratio of the specific heat of the gas at constant pressure to its specific at constant volume. Now if this given mass of gas is allowed to expand indefinitely, or until its volume becomes infinite, the total amount of work it can do is

$$Work = \int_{v_0}^{\infty} p \,.\, dv. \tag{19}$$

If we substitute in this equation the value of p as obtained from (18), and perform the integration, we have

$$Work = \frac{p_0 v_0}{\gamma - 1}. \tag{20}$$

Now the work that a gas can do under such circumstances (assuming that there are no forces between the molecules) is equal to its total kinetic energy, k_0. Equating k_0 to the second member of (20), we have

$$p_0 v_0 = (\gamma - 1)\, k_0, \tag{21}$$

and comparing this with equation (16) we see that

$$\gamma - 1 = \frac{2}{n}, \quad \text{or} \quad \gamma = 1 + \frac{2}{n}. \tag{22}$$

From this equation we can calculate the ratio of the specific heats of a gas, if we know n, the number of degrees of freedom of its molecules; and conversely, we can calculate from it the number of degrees of freedom of the molecules, if we know the ratio of the specific heats of the gas. Now the smallest value that n can have is three; for it must take at least three coördinates to fix the position of a body in space. The value $n = 3$ corresponds to the case in which the molecules are smooth spheres, incapable of being set in rotation by their mutual impacts. Mercury, for chemical reasons, is believed to contain only one atom in its molecule; and hence it will be interesting to see whether the ratio γ, calculated on the hypothesis of a smooth, spherical molecule, corresponds with the actual value of this ratio for mercury vapor. We find, for $n = 3$, $\gamma = 1\frac{2}{3} = 1.66\dot{6}$; and the ratio of the specific heats of mercury vapor, as determined experimentally by Kundt and Warburg, is 1.66. The agreement of this with the calculated value lends considerable plausibility to the supposition that the molecules of mercury are smooth and spherical, and, incidentally, to the whole kinetic theory. In the case of other gases the agreement is not so satisfactory. For example, the molecules of hydrogen, oxygen, nitrogen, and carbonic oxide, are believed, for chemical reasons, to consist of two atoms. We are led, naturally, to examine the results of the hypothesis that their molecules each consist of two smooth, spherical atoms, rigidly united by attractive forces or otherwise. The number of degrees of freedom that we have to

consider in such a system is 5 (the freedom to rotate about the line of centers of the spheres is not considered, because as the spheres are assumed to be perfectly smooth the impacts of the molecules cannot set up rotations about this axis). When $n=5$, we have $\gamma=1+\frac{2}{5}=1.400$. The accepted values of γ for these gases, as given by experiment,* are presented in this table:

TABLE OF VALUES OF γ.

GAS.	EXPERIMENTAL γ.	CALCULATED γ.
Oxygen	1.402	1.400
Nitrogen	1.411	1.400
Hydrogen	1.412	1.400
Carbonic oxide	1.418	1.400

At first thought this seems like a very satisfactory agreement; but it is not so. We have assumed, in deducing equation (22), that the effects of the intermolecular forces are insensible; but it can be shown that if they were sensible we should have to modify equation (22) so as to make it read

$$\gamma=1+\frac{2}{n+x}$$

where x is a small *positive* quantity, vanishing when the forces between the molecules are insensible. You will please note particularly that x is necessarily *positive* if the forces are attractive, so that the calculated values of γ would be *smaller*, if we take these forces into account, than it would be if we neglected them and considered x to be zero; whereas the observed fact is, that the values of γ are *larger* than the computed value obtained by making $x=0$. This constitutes an objection to the kinetic theory, which is worthy of serious consideration. Mathematicians have endeavored to account

* These experimental results are from the *Encyclopædia Britannica*, article *Steam Engine*.

for the observed discrepancy in various ways, but without any very distinguished success. You will find a suggestion made in Mr. Watson's little book on the kinetic theory of gases ; but as it involves some rather intricate considerations, and cannot be regarded at present as anything *more* than a suggestion, I shall not trouble you with it this evening. I have an idea that the true explanation will be found to involve the consideration of gaseous *dissociation.* It is known that many gases exhibit this phenomenon in a marked degree when their temperature is sufficiently high. According to what I have told you, raising the temperature of a gas is really the same thing as accelerating its molecules. When the mean speed of the molecules reaches a certain value, the shocks due to the molecular collisions become so great that the internal attractive forces existing within the molecules are no longer sufficient to hold them together. They break up, therefore, into simpler molecules, or perhaps into their constituent atoms. This phenomenon is known as *dissociation.* Owing to the great variety of velocities that exist within any given mass of gas, the dissociation does not take place suddenly, when the gas reaches a particular temperature. If the temperature of the gas be gradually raised, there will come a time when a considerable number of the molecules possess the velocity requisite for dissociation, although the great mass of them may still have velocities that are considerably below this critical value. Dissociation then commences. If the temperature of the gas be now kept constant the dissociation does not proceed until the molecules are all split apart, because many of the dissociated parts, coming together again at velocities less than the critical velocity, re-combine and produce new molecules like those of the original gas. You will see, therefore, that at any given temperature dissociation proceeds only until there is an equilibrium established between the molecules that are breaking up, and those that are re-forming. If the temperature be now raised, the average velocity will come nearer to the

critical value, and when equilibrium has been established at this new temperature, the number of molecules that exist in the dissociated condition at any given instant will be greater than before. If the temperature be high enough, the number of dissociated molecules that happen to collide, during any given time, with velocities sufficiently small to allow of re-combination, may be so insignificant that we cannot recognize the presence of these re-combined molecules by any of the chemical or physical tests at our command. The gas is then said to be wholly dissociated. Now it seems probable that in *any* gas there must be *some* molecules in a state of dissociation, even though the temperature may be far below the critical value conventionally called the temperature of dissociation; for we have seen that in any given mass of gas there are always some few molecules moving with extreme velocities — velocities great enough to produce dissociation. We may therefore conceive hydrogen gas, for example, to be an aggregation of molecules, by far the greater number of which are diatomic with 5 degrees of freedom, but some of which, nevertheless, are monatomic with 3 degrees of freedom. The value of γ for such a gas would be intermediate between the value calculated for $n = 5$ and that calculated for $n = 3$; or in other words, it would lie between 1.400 and $1.66\dot{6}$, but far nearer the former value than the latter. It seems to me that the calculated and observed values of γ can be reconciled in this way, but before we could prove this to be the fact we should have to make a rigid mathematical investigation of the theory of dissociation. If this be the true explanation, it is evident that the value of γ must increase when the temperature of the gas increases; for at higher temperatures there would be a greater proportion of dissociated molecules present. I know of no experiments sufficiently accurate to test this point. There is, of course, a possibility that the *observed* values of γ are incorrect, owing to the existence of some unrecognized source of error tending to give results uniformly too great; but this would have to be *proved* to be the fact

before we could accept it as the true explanation of the difference between calculation and observation. The ratio of the specific heats of gases is usually calculated from the velocity of sound as observed in the gases; and as the necessary measurements are difficult to make, we find that with different data different results are obtained. Thus from Dulong's data for dry air we have $\gamma = 1.410$, while from the data for air as given by Regnault and Poisson, we find $\gamma = 1.401$. So far as the gases in the table are concerned, it is worthy of note that a recent determination of γ for hydrogen (given by Clausius and quoted in Watts's *Dictionary*) gives $\gamma = 1.3852$. I also find that if the value of γ be calculated by combining the specific heat at constant pressure as observed by Regnault, with the difference between the specific heats as calculated by Rankine's method, we have, for oxygen, $\gamma = 1.398$; using Regnault's results for the density of oxygen, Thomson's determination of the absolute zero, and Griffiths's value of the mechanical equivalent of heat.* In view of the differences that exist among the different experimental determinations of γ, I think it would be unwise to conclude that the present discrepancy between the kinetic theory and the apparent facts may not be cleared up satisfactorily in the future. We must note, however, that since 3 is the smallest number of degrees of freedom that a free body in space can have, it follows from (22) that $\gamma = 1\frac{2}{3}$ is the largest ratio of the specific heats that the kinetic theory is capable of explaining. If it can be shown that the ratio of the specific heats of any gas is greater than this, it looks as though the kinetic theory would have to go. You may be interested to know that for highly superheated steam the value of γ is 1.30. This seems to correspond to a molecule with 6 degrees of freedom; for with this value of n, equation (22) gives $\gamma = 1.33\dot{3}$. The observed value of γ for carbonic acid gas is 1.263, which seems to indicate 7 degrees of freedom; for

* The same method gives for H, $\gamma = 1.408$; and for N, $\gamma = 1.407$. See Appendix.

when $n = 7$ equation (22) gives us $\gamma = 1.286$. These values of n, for steam and for CO_2, seem to indicate that steam molecules are rigid bodies, and that the molecules of CO_2 may consist of two smooth bodies jointed together in some way; but in speculating in this manner on the actual forms of the molecules we are going a good way beyond the limits of positive knowledge.

Molecular Attraction in Gases. — Thus far we have assumed that the molecules of a gas do not attract one another, but that the phenomena of gases result from the motions of the molecules, unrestrained except by their collisions with one another and with the walls of the containing-vessel. It appears, from the agreement of the results of this assumption with the observed facts, that the effects of the mutual attractions that may exist between the individual molecules of a gas are small, on the whole. The forces, when they exist, may be great; but since their effects are scarcely noticeable, we must conclude that under ordinary circumstances the sphere of sensible action of these forces is quite small in comparison with the length of the average free path of the molecules. We may investigate the attraction or repulsion that may exist between gaseous molecules, by allowing a given gas to expand into a vacuum so that it shall do no external work. If there is an attraction between the molecules, the gas will be cooled; for some of its kinetic energy will be transformed into potential energy. The experiment being performed, it is found that there is almost no change in temperature produced by simple expansion, when the gas does no external work. Very accurate experiments by Thomson and Joule, however, showed that there is a *slight* temperature change, though it is so small that it could readily escape observation. In order to avoid eddies and other such sources of error, Joule and Thomson caused the gases they experimented upon to flow from one vessel into the other through a porous plug.* The

* *Encyclopædia Britannica*, article *Heat.*

initial pressure, in their experiments, ranged from 1 up to 5 or 6 atmospheres, the final pressure being 1 atmosphere in every case; and the cooling effect was found to be proportional to the difference between the initial and final pressures. In the case of air, the cooling effect was 0°.208 C. per atmosphere. With carbonic acid gas it was 1°.105 C. With hydrogen, on the other hand, there appeared to be a *heating* effect of °.039 C. per atmosphere. (Owing to its peculiar behavior, Regnault called hydrogen *un gaz plus que parfait*— "a more than perfect gas.") These experiments show that there are attractive forces between the molecules of air, and also between those of carbonic acid gas. In expanding, the molecules of these gases have become more widely separated, and energy that was before *kinetic*— and therefore sensible as heat— has become *potential* in overcoming the attractive forces. The behavior of hydrogen is anomalous. No other gas exhibits a heating effect when expanding into a vacuum. The discussion of this isolated phenomenon would take so much time that I shall not enter upon it this evening. We must note that the cooling effect observed by Joule and Thomson affords a rough indication that the attraction between gaseous molecules does not follow the inverse-square law with which we are so familiar in the laboratory and the observatory. It indicates, in fact, that the attraction varies something like the inverse fourth power of the distance. For let us assume that the law of attraction is

$$f = \frac{a}{D^4} \tag{23}$$

where D is the mean distance between two neighboring molecules. Then if the gas expands until this mean distance becomes D_1, we may express the work done against the attractive forces somewhat as follows:

$$Work = \int_D^{D_1} f \cdot dD = a \int_D^{D_1} \frac{dD}{D^4} = \frac{a}{3}\left(\frac{1}{D^3} - \frac{1}{D_1{}^3}\right). \tag{24}$$

Now, as D is a linear dimension in the gas, the volume of the gas will vary as the *cube* of D. Hence, we may write

$$v = b \cdot D^3\,, \text{ and } v_1 = b \cdot D_1^3.$$

Substituting, in (24), the values of D^3 and D_1^3, as given by this equation, we have

$$Work = \frac{ab}{3}\left(\frac{1}{v} - \frac{1}{v_1}\right). \tag{25}$$

But as the temperature of the gas is practically constant, we have

$$pv = p_1 v_1 = c\,.$$

Substituting, in (25), the values of v and v_1, as given by this equation, we have, finally,

$$Work = \frac{ab}{3c}\,(p - p_1)\,.$$

That is, the assumed law of attraction* indicates that when a gas expands into a vacuum, the amount of work done in overcoming the internal attractive forces — or, what is the same thing, the amount of kinetic energy that disappears and ceases to be sensible as heat — is proportional to the difference between the initial and final pressures; and this is the observed fact. I am aware that equation (24) is only a crude expression for the amount of internal work, and that consequently the reasoning I have given you does not prove that the inverse fourth-power is the true law of variation of intermolecular attraction; but I think it is fair to say that the reasoning shows, at least, that when two molecules approach each other, the attraction between them increases faster than the inverse-square law would indicate. Although the reasoning I have given you does not prove that equation (23) represents the true law of molecular attraction, Mr. William Sutherland has recently shown, in a more rigorous manner, that this is very likely the fact.† I may, perhaps, venture

* See equation (23).

† See his recent articles in the *Philosophical Magazine.*

the suggestion (though it has never yet been proven) that the attraction existing between the molecules of a gas is due to the same ultimate cause as gravitational attraction (whatever that cause may be), and that the so-called Newtonian law of inverse squares is only an approximate expression for the relation between gravitation and distance, which is sensibly accurate only when the distance, D, greatly exceeds the dimensions of a molecule. If this conjecture be correct, the true law of gravitational attraction is probably a function capable of development in terms of descending powers of D, thus :

$$f(D) = \frac{a}{D^2} + \frac{b}{D^3} + \frac{c}{D^4} + \dots \tag{26}$$

where the terms after the first have very small coefficients, so that they are insensible except when D is itself extremely small, and the reciprocals of its higher powers correspondingly large.

Equations of Van der Waals and Clausius.—The equation

$$pv = R\tau \tag{27}$$

being deducible from the kinetic theory only when the assumption is made that the effects of the attractive forces between the molecules are insensible, and it being admitted that even in the so-called permanent gases these forces are not *absolutely* insensible, it would naturally be expected that accurate observations would show that this equation is not perfectly fulfilled by any gas. And it is so. We can no longer regard this simple law as anything more than a very good first approximation to the truth. All gases exhibit variations from it, and these variations are quite marked at high pressures, when the molecules are crowded closely together. Many formulæ have been proposed as "second approximations," and of these the most famous is undoubtedly that given by Van der Waals, over which there has been much controversy. It will be evident to you, I think, that

the "volume" entering into our expressions should not be, strictly speaking, the actual space occupied by the gas, but rather the space in which the molecules are free to move; that is, the *empty* space within the enclosure, or the space not actually filled by the molecules themselves. We may therefore use the expression $(v-b)$ in the place of v in the foregoing formula, v still signifying the apparent volume of the gas, while $(v-b)$ is the empty part of it. The gas equation will then read

$$p\,(v-b)=R\tau,\ \text{or}\ p=\frac{R\tau}{(v-b)}\,. \tag{28}$$

This formula is an improvement on the older one, but we have not yet taken account of the attractive forces between the molecules. If we should compress a gas, we should be assisted by this internal attraction; and therefore the actual external pressure required to reduce the volume by a given amount would be less than that calculated by either (27) or (28). This much, I think, is admitted by all physicists; but there is a considerable disagreement among them as to the actual algebraic form of the correction thus called for. Van der Waals considered it to be expressible by a term of the form $\frac{a}{v^2}$; and his equation is, therefore,

$$p=\frac{R\tau}{(v-b)}-\frac{a}{v^2},\quad \text{or}\quad \left(p+\frac{a}{v^2}\right)(v-b)=R\tau. \tag{29}$$

Clausius proposed, in the place of $\frac{a}{v^2}$, the expression

$$\frac{c}{\tau\,(v+\beta)^2},$$

so that his equation is:

$$p=\frac{R\tau}{(v-b)}-\frac{c}{\tau\,(v+\beta)^2}\,. \tag{30}$$

However interesting Van der Waals's equation may be, it certainly does not represent the facts of observation satis-

factorily, unless we cease to regard a and b as constants. Clausius's equation, on the other hand, is found to represent the results of Andrews's extensive experiments on CO_2, with great fidelity. The values of the constants, in (30), for CO_2 are as follows:

$$R = .003688, \qquad b = .000843,$$
$$c = 2.0935, \qquad \beta = .000977.$$

The pressures are to be reckoned in atmospheres, the temperature is to be measured on the absolute Centigrade scale, and the unit of volume is the volume of the gas itself at the freezing-point, and at atmospheric pressure.

Diffusion. — There are two properties of gases to which I must refer before passing to the consideration of liquids. The first of these is *diffusion*. It has often been remarked, by persons not conversant with the kinetic theory, that if the molecules of gases are moving at the rate of thousands of feet per second, it is hard to understand why one gas does not diffuse through another with correspondingly great rapidity; so that if a bottle of some strong-smelling gas, like ammonia, were opened in one part of a room we could smell it in another part without any sensible lapse of time, even if the air of the room were, apparently, at perfect rest. The answer to this is, that although the molecules of ammonia vapor do have high velocities, they cannot travel in uninterrupted straight lines across the room, like projectiles, because there are enormous numbers of air molecules in the way, with which they collide thousands of millions of times in a second. In a rough way, the case may be likened to an army of swift runners trying to pass, at the top of their speed, across a field thickly set with posts. Of course this is a very crude comparison, but it may serve to fix the idea. The runners would be merely turned aside, first one way and then another; but the ammonia molecules, rebounding from the air molecules that they strike, are actually turned about, and in

such diverse directions, that in any given region there are almost as many of them returning towards the bottle as there are going away from it. They are forced to describe zig-zag paths which are so very crooked that by the time a given ammonia molecule has reached a point actually ten feet distant from the bottle, it has traveled, in all, an enormously greater distance — probably quite a number of miles. I shall not give you the mathematical theory of diffusion, because it is very much involved. Furthermore, I do not consider that any very valuable information has yet been obtained from it. I say this with all due respect to the men who have worked over this theory so patiently. What they have learned about diffusion has been found out by great labor, and it is gratifying to know that the results of this labor accord well, in general, with similar results obtained by other methods. There is no doubt that very important facts will be learned, some day, from the study of diffusion, and I should not want to discourage any of you who may feel disposed to enter the lists and give battle to the formulæ involved.

Viscosity.—The other property of gases to which I referred a moment ago is *viscosity*. It is by no means an obvious property, and its effects are quite small — so small, in fact, that they are difficult to measure with precision. You are probably better acquainted with the viscosity of liquids than you are with the corresponding property of gases. Molasses and maple syrup are familiar examples of viscous liquids. You will understand that if two planes were submerged in molasses, and one of them was caused to move in its own plane, parallel to the other one and near it, there would be a certain drag exerted on the motionless plane, tending to pull it in the direction in which the first plane is moving. This "drag" would also be experienced by the fixed plane if any other liquid were substituted for the molasses; and it is found that the same effect is observable, though in a much

smaller degree, even when the experiment is performed with gases instead of with liquids. This property of fluids, in virtue of which they can transmit motion from one moving plane to another one parallel to it, is called *viscosity*. In many respects viscosity is analogous to friction; and physicists (particularly among the Germans) often call it the "internal friction" of the fluid. In Fig. 21, A represents the moving plane, and B the fixed one. If the fluid between them be conceived to be divided into exceedingly thin layers, as suggested in the diagram, we may conceive the resistance

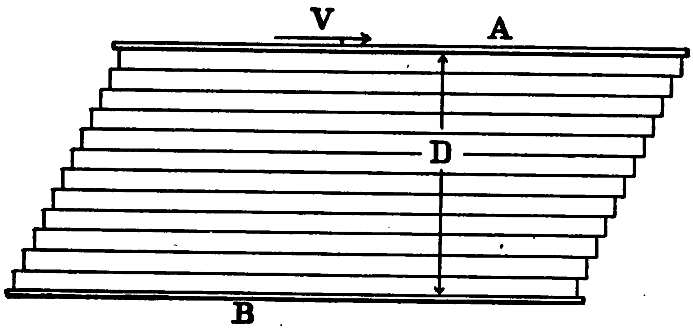


FIG. 21. — DIAGRAM ILLUSTRATING VISCOSITY.

to the motion of A to be due to the friction of these layers upon one another. If F is the force required to overcome this friction — or, which is the same thing, if F is the force required to sustain the motion of A, — it may be shown* that

$$F = \frac{\mu S V}{D},$$

where S is the area of the plane A, V is its velocity, D is the perpendicular distance between A and B, and μ is a coefficient peculiar to the fluid experimented with, and called its *coefficient of viscosity*.

* See *Encyclopædia Britannica*, article *Hydro-mechanics*, part III.

Experimental Determination of μ. — The foregoing equation may be written in the form

$$\mu = \frac{DF}{SV}. \tag{31}$$

Hence the coefficient of viscosity of a fluid can be determined, if we can measure the quantities D, F, S, and V. The only one of these that presents the least difficulty is F, which, for gases, is so small that its determination is extremely difficult. Various methods have been tried, however, and owing to the skill and patience of the experimenters, the results are fairly satisfactory. Meyer determined F by a study of the action of air on vibrating pendulums. He worked with three pendulums, and considered that the most trustworthy result was that obtained from the shortest one of the three. The value of F thus deduced by him gave

$$\mu = .000184,$$

the units being the centimeter, gramme, and second.

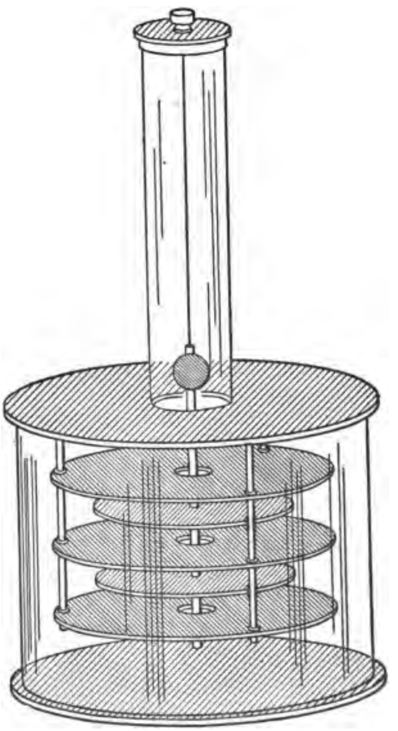


FIG. 22. — DIAGRAM ILLUSTRATING MAXWELL'S APPARATUS.

Another method, tried with success by Maxwell (and Meyer also), consisted in causing a circular disk to oscillate in its own plane, between two

others that were parallel to it. The way in which the oscillations died out gave a means of calculating F, and then, by substitution in (31), the value of μ was obtained. In the actual experiment, Maxwell used several disks fixed to a common axis, instead of only a single one. Fig. 22 is a diagram illustrating the principle of his apparatus.* Maxwell's final result for the coefficient of viscosity of dry air was

$$\mu = .0001878\,(1 + .00365\,t).\dagger$$

Meyer's result was

$$\mu = .000190\,(1 + .0025\,t).$$

In both of these expressions t is the temperature, on the Centigrade scale, counted from the freezing point of water in the usual way. Maxwell's expression, as quoted above, implies that μ varies directly as the absolute temperature. Meyer found, by experiment, that it varies in proportion to the .77 power of the absolute temperature. That is, it varies proportionally to

$$\left(\frac{t_0 + t}{t_0}\right)^{.77} = \left(1 + \frac{t}{t_0}\right)^{.77} = 1 + .0028\,t$$

where $t_0 = 273°$, or the absolute temperature of the freezing point on the Centigrade scale. The best value of the coefficient of viscosity of dry air at present obtainable is considered by Knott ‡ to be

$$\mu = .000185\,(1 + .0028\,t). \tag{32}$$

Professor Knott also gives a table of the relative values of the coefficients of viscosity of other gases, as determined by Graham, Maxwell, Meyer, Kundt and Warburg, and Crookes.

* For an engraving of the actual apparatus, see the *Philosophical Transactions of the Royal Society of London*, for 1866.

† In all that is said in this volume about viscosity, the fundamental units are understood to be the centimeter, gramme, and second.

‡ *Encyclopædia Britannica*, article *Pneumatics*.

From this table we may perhaps infer the following relative and absolute values of the coefficients of viscosity of these gases, at the freezing point of water:

TABLE OF COEFFICIENTS OF VISCOSITY OF GASES.

GAS.	COEFFICIENT OF VISCOSITY.	
	Relative.	Absolute.
Air	1.000	$\mu = .000185$
Oxygen	1.109	.000205
Nitrogen	.972	.000180
Hydrogen	.484	.000090
Carbonic Oxide	.970	.000179
Carbonic Acid	.855	.000158

Kinetic Explanation of Viscosity. — Returning to our conception of a gas as an aggregation of swiftly moving molecules, let us see if it is not adequate to explain the viscosity that experiment has shown these bodies to possess. Referring back to Fig. 21, let us conceive the imaginary layers of gas there represented to be of such a thickness that the average "free path" of the molecules of the gas will be just sufficient to allow these molecules to cross one layer in the interval between two successive collisions. Now when the molecules in the upper layer strike against *A*, they receive from it a component motion in the direction of the arrow. Rebounding from *A*, they cross the first layer and collide with the molecules of the second layer, communicating to them also a component motion in the direction of the arrow. The molecules in the second layer carry this component over to those in the third layer, and so on until the molecules in the last layer tend to communicate a component motion, in the direction of the arrow, to the plane *B*. This is the general nature of the kinetic explanation of viscosity in gases, though you will understand that in the rigorous mathematical

treatment of the subject it is necessary to take account of many things that I have not mentioned; such, for instance, as the law of distribution of velocities among the molecules. Several mathematicians, following out the general idea I have given you, have deduced from the kinetic theory of gases, expressions for the coefficient of viscosity. One of the most recent of these expressions is that of Clausius, which is

$$\mu = 20.23\,\lambda\,\sqrt{\Delta}\sqrt{\frac{T}{T_0}}, \tag{33}$$

where Δ is the density of the gas at 0° C. and atmospheric pressure, as compared with air under the same conditions, T is the absolute temperature of the gas, T_0 is the absolute temperature of the freezing point of water (273° C.), and λ is the average "free path" of the molecules of the gas, at atmospheric pressure and at 0° C. While it is true that this formula does not accurately represent the experimental facts, inasmuch as the exponent of the absolute temperature is known to be about .77 instead of $\frac{1}{2}$, the error introduced in this way is practically insensible for temperatures near the freezing point.* There is one very important thing I would like you to notice about this formula. It is, that the formula indicates that the coefficient of viscosity of a gas remains unchanged, *no matter how much we rarefy the gas or compress it;* for λ and Δ are constants, since they stand for the free path and density *at atmospheric pressure and at 0° C.* That

* Mr. Sutherland has shown very clearly that the difference between theory and experiment, here mentioned, disappears if we take account of the attractive forces existing between the molecules of the gas. Assuming that these forces are proportional to the inverse fourth-power of the distance, he finds that

$$\frac{\mu}{\mu_0} = \sqrt{\frac{T}{273}} \cdot \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}}$$

where μ_0 is the coefficient of viscosity at the freezing point and μ is the corresponding coefficient at the absolute temperature T. The value of

the viscosity of a gas does not depend upon its absolute density, has been amply verified by experiment. Numerous observers have found that air at a pressure of only a few millimeters of mercury has substantially the same viscosity as air under the normal pressure of 760 millimeters. It is hardly necessary to say that this constitutes a most remarkable verification of the kinetic theory. Of course this statement about viscosity being independent of absolute density must not be pressed to extremes, or we should be saying that a vacuum has just as much viscosity as common air; which would be absurd. A vacuum cannot have viscosity. This does not involve an error in Clausius's reasoning, however, for, as he says himself, his formula was deduced on the assumption that the free path is so small that terms involving higher powers of it than the first can be neglected. There is no doubt about this being the fact under ordinary conditions; but when the gas is rarefied the molecules have much more free space to move in. They do not collide so often, and hence their average free path becomes greater. As the exhaustion proceeds, there comes a time when the terms involving powers of the average free path higher than the first cannot be neglected; and when that point is reached, the formula no longer has any pretensions to accuracy.

the constant C, for CO_2, is 277. The following table exhibits the agreement of this formula with Holman's experiments on CO_2:

TABLE OF VALUES OF THE RATIO $\frac{\mu}{\mu_0}$ FOR CO_2.

TEMP.	OBSERVED RATIO.	CALCULATED RATIO.	TEMP.	OBSERVED RATIO.	CALCULATED RATIO.
18° C.	1.068	1.066	119°.4 C.	1.415	1.414
41°	1.146	1.148	142°	1.484	1.490
59°	1.213	1.211	158°	1.537	1.541
79°.5	1.285	1.280	181°	1.619	1.614
100°.2	1.351	1.351	224°	1.747	1.746

Free Path. — Clausius's formula is of no particular value for computing the coefficient of viscosity of gases, because it involves the free path, λ, which is much harder to determine than the viscosity is; but when the coefficient of viscosity has once been determined *by experiment*, Clausius's formula becomes of the most extreme importance for the inverse problem of *determining the average free path.* Thus, confining our attention to the case in which $T = T_0$, we may write the formula in the form

$$\lambda = \frac{\mu}{20.23\sqrt{\Delta}}. \qquad (34)$$

Applying this equation to carbonic acid gas, for which $\Delta = 1.529$ and $\mu = .000158$, we have

$$\lambda = \frac{.000158}{20.23\sqrt{1.529}} = .000\,0063 \text{ cm.}$$

Similar calculations for the other gases whose coefficients of viscosity are in the table I gave you a few moments ago, give the following results:

TABLE OF AVERAGE FREE PATHS AT ATMOSPHERIC PRESSURE AND 0° C.

GAS.	DENSITY. (Air = 1.)	AVERAGE FREE PATH.	
		Centimeters.	Inches.
Air*	1.0000	.000 00914	.000 0036
Oxygen	1.1056	.000 00964	.000 0038
Nitrogen	.9713	.000 00903	.000 0036
Hydrogen	.06926	.000 01690	.000 0067
Carbonic Oxide	.9545	.000 00906	.000 0036
Carbonic Acid	1.5290	.000 00631	.000 0025

I think these figures will make it plain why one gas does not diffuse through another with a speed comparable with the velocity of translation of its molecules. Consider the case of

* Calculated as a simple gas.

hydrogen, for example. We found the average velocity of translation of its molecules to be 5,571 feet per second; and as the average free path of its molecules, between collisions, is .000 0067 of an inch, you will see that, on an average, each of its molecules experiences

$$\frac{5{,}571 \times 12}{.000\,0067} = 10{,}000{,}000{,}000\,*$$

collisions with its neighbors every second. When one gas is diffusing through another one, the calculation is not so simple; because in that case there are two kinds of molecules to be considered, and we must take account of the collisions of each molecule with those of its own set, and with those of the other set. Still, I think you will be quite ready to admit, from the calculation I have given you in the case of hydrogen, that the number of collisions per second experienced by each of the molecules of a diffusing gas would be so great that the explanation of the slowness of diffusion that I offered you a few moments ago is quite defensible. It may interest you to know the average number of collisions per second experienced by a molecule in some other gases. I have therefore calculated this table, by the same method used in the case of hydrogen, and from the data concerning the free paths and the molecular velocities that have already been placed before you.

Table of the Average Number of Collisions per Second Experienced by a Molecule of Various Gases, at Atmospheric Pressure and 0° C.

Gas.	Collisions per Second.
Oxygen	4,410,000,000
Nitrogen	5,021,000,000
Hydrogen	10,040,000,000
Carbonic Oxide	5,014,000,000
Carbonic Acid	5,741,000,000

* In round numbers.

High Vacua. — The average free path of the molecules of a given gas is independent of the *temperature*, but it varies when the *density* of the gas is made to vary. For the average distance a molecule will travel, between successive collisions, will obviously be less when there are many molecules in a unit volume than it will be when there are but few of them. In fact, mathematical analysis shows that the length of the average free path is exactly proportional to the reciprocal of the density of the gas. It follows from this that we can make the average free path as great as we please, by diminishing the density of the gas sufficiently. If, therefore, we should diminish the density by the aid of a good modern air pump until it were only (say) a millionth of its normal value at atmospheric pressure, we should thereby increase the average free path of the molecules to one million times the lengths I have given you in the table.* Thus in the case of CO_2 the average free path would become about two inches and a half, and in the case of hydrogen it would even become six inches and three-quarters. It would be natural to think that at such high exhaustions the residual gas would exhibit no phenomena at all — that it would be indistinguishable from a vacuum. But this is not the case. We must remember that the contents of a vessel exhausted to this degree is called a vacuum "by courtesy only." There are still many millions of molecules left in it; and as their mean free paths are now measurable in *inches*, the medium exhibits entirely new properties, some of which I shall try to show you.

The Radiometer. — I have here a small piece of apparatus (Fig. 23), kindly loaned for the evening by Professor Kimball, from the physical laboratory of the Institute. You will see that it consists of a glass bulb in which is a sort of wind-mill, mounted very delicately upon a pivot. The vanes of this wind-mill are blackened on one side, while on the other side they are bright. I will hold the bulb near the gas jet.

* On page 66.

You see that the vanes are now flying around very rapidly, bright side foremost. I hold it still nearer the gas jet, and the vanes revolve with such speed that they cannot be separately distinguished. This wonderful little instrument is called the *radiometer;* and I am going to try to make it clear to you why the vanes revolve. The ultimate phenomena on which the motion depends are somewhat complicated, and I shall only attempt to give you a general idea of them.* In the first place, the blackened sides of the vanes absorb more of the radiant energy from the gas jet than the bright sides do, and hence they become warmer. This difference in temperature is essential to the working of the instrument; and hence it is important to make the vanes of some fairly good non-conductor, such as mica, in order that the temperatures of their opposite surfaces may not become equalized by conduction. The difference in temperature between the black and bright surfaces is probably small, but for brevity we may speak of these surfaces as the "hot side" and the "cold side," respectively. The molecules on the hot side of a vane are vibrating more energetically than they are on the cold side and hence they communicate heavier blows to such gas-molecules as chance to collide with them. Now, since action and reaction are equal, it follows that the gas-molecules react more powerfully on the hot (or black) surfaces than they do

FIG. 23. — THE RADIOMETER.

* For a more satisfactory discussion, see Maxwell's article in the *Philosophical Transactions* for 1879.

on the cold ones, and hence there is a tendency to drive the vanes around as you saw them go, bright side foremost. This tendency is not sufficient to cause the vanes to revolve when the bulb is filled with air of ordinary density, however, because the average free path of the air-molecules is so extremely small, and the number of molecular collisions per second so enormously great, that the accelerated molecules that fly off from the hot sides of the vanes beat back the molecules of air in the immediate neighborhood of the vane sufficiently to cause a slight rarefaction of the air in front of the hot side. This rarefaction tends to make the vanes revolve *black* side foremost. When the air in the bulb is of ordinary density, these two opposing tendencies appear to be sensibly balanced, and no motion results. When the air in the bulb is moderately exhausted, the effect due to local rarefaction in front of the hot side preponderates, and the vanes slowly revolve *black side foremost;* but when the exhaustion is pushed to such a degree that the free path of the residual molecules becomes as great as the distance from the vanes to the glass bulb, the accelerated molecules no longer beat back their neighbors; there is no local rarefaction; the only remaining cause of motion is the reaction of the black surfaces against the accelerated gas-molecules; and the vanes therefore revolve *bright side foremost.*

Crookes's Tubes.—The radiometer depends for its action on the presence of the walls of the glass bulb, and the larger the instrument is, the more perfect must the exhaustion of the bulb be; for the essential thing about the instrument is, as I have explained, that the average free path of the molecules of the residual gas must be great enough to permit these molecules to strike against the walls of the bulb, after rebounding from the vanes, instead of against one another. I have here three other pieces of apparatus, the operation of which does *not* depend upon the dimensions of the containing tube. I am enabled to show you these tubes through the

courtesy of Messrs. Queen & Co., of Philadelphia, to whom they belong, and who have very kindly loaned them for this occasion. In each of these tubes the degree of exhaustion is so great that the average free path of the residual molecules is several inches long. I will first show you this tube (Fig. 24), in which the vanes of the little fly are set obliquely, and are not blackened at all. As I connect the terminals of the battery with the ends of the loop of wire below the fly, you notice that this wire becomes hot. The gas-molecules that collide with the hot wire are driven off in all directions, at greatly increased speed, by the vigorous blows they receive from the molecules of the wire, which are now vibrating very energetically. Those that strike against the vanes of the fly impinge on them obliquely and cause them to revolve, as you see they are now doing. I will next connect the loop and the upper electrode with the respective terminals of the induction coil. You see that this also causes the fly to rotate. Before explaining why the induction coil causes the vanes to move, I will show you another tube (Fig. 25), which is very simple in construction, but very beautiful and instructive in operation.* It consists of two electrodes sealed into the tube, one of which is concave, or cup-shaped. As I throw the coil into action, you notice the hazy double cone of purplish light, the vertex of which is at the center of cur-

FIG. 24.—A CROOKES'S TUBE WITH OBLIQUE VANES.

* In exhibiting this tube and the next one, the lights in the lecture room were turned down.

vature of the concave electrode; and where the cone spreads out so as to intersect the outer tube, the glass shines with a beautiful golden fluorescence. Now the explanation of this phenomenon is, that as the molecules of residual gas come in contact with the concave electrode they receive a charge of electricity themselves, and are energetically repelled in a direction normal to the surface of the electrode. Flying away from the electrode, they necessarily pass close to its center of curvature, and being crowded together at that point, they brush against one another sufficiently to give rise, in some manner, to the purplish glow that you see. After they

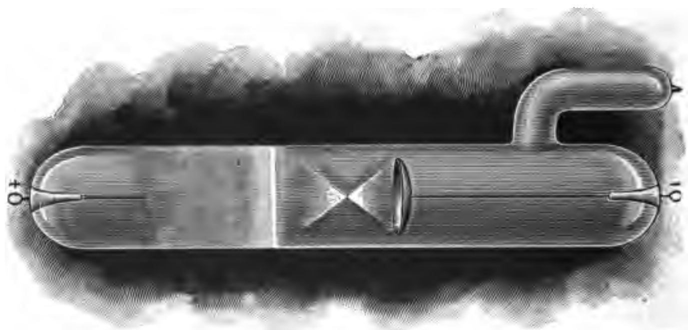


FIG. 25. — A CROOKES'S TUBE WITH CONCAVE ELECTRODE.

have passed the vertex of the cone of light, they diverge once more; and when, continuing to move in straight lines, they come in collision with the sides of the tube, they excite a fluorescence in the glass which dies away towards the remote end of the tube, as the flying stream of molecules strikes more and more obliquely. I think you will see, now, why the induction coil caused the vanes of the other tube (Fig. 24) to revolve. The gas-molecules were projected from the electrode by electrical repulsion, and the effect was the same as when the wire loop was directly heated by the battery. There is one very strange thing about these high vacuum tubes, which I think no one has yet satisfactorily explained.

You will notice that when I reverse the direction of the current through the coil, the appearance of the tube (Fig. 25) is entirely changed. There is no longer any sign of the double cone of flying molecules. It appears that in the phenomena of electric repulsion in these tubes, it is the negative electrode *exclusively* that is concerned. It seems to make little difference what part of the tube the positive electrode is in. I will now show you the remaining tube (Fig. 26), and I think you will agree with me that it is exceedingly beautiful when in operation. It consists of a horizontal tube containing a pair of parallel glass rails, along which a sort of little paddle-wheel can roll. The electrodes, you will notice, are on a level with the uppermost vanes of the wheel. I will now

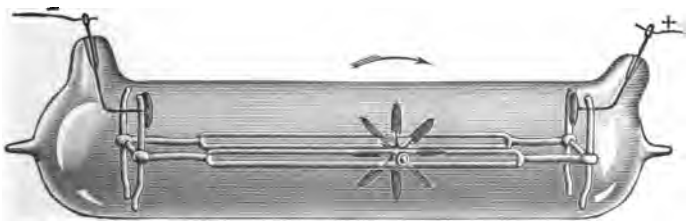


FIG. 26. — A CROOKES'S TUBE WITH ROLLING WHEEL.

start the coil in action, and you see the whole tube glorious with light and color. The molecular stream from the negative electrode, beating on the upper vanes, causes the wheel to revolve and roll along the track toward the other end of the tube; but just before it gets there I reverse the coil, and you see the wheel come to a stand-still and then begin to revolve in the opposite direction until it returns to its starting point. We can make it travel back and forth as many times as we please, by merely reversing the coil when the wheel nears the end of its course. You will notice, at the ends of the tube and along the bottom of it, what appears to be the shadow of the glass rails. It is not a true shadow, however. The gorgeous fluorescence that you see elsewhere is caused, as in the last tube I showed you, by the impact of the molecules

against the sides of the tube; and the dark places do not shine, simply because they are shielded from the molecules that are streaming away in straight lines from the negative electrode. To prove this to you, I move this small magnet about in the neighborhood of the tube, and you see the dark lines shifting from place to place, as they would not do if they were true shadows. The streams of electrified molecules, behaving in a certain sense like electric currents, are deflected by the magnet; and different parts of the tube are shielded as I change the magnet into different positions, so that the pseudo-shadows appear to move about. Before leaving this interesting subject, let me say that these wonderful mechanical phenomena in high-vacuum tubes were discovered by Mr. William Crookes, whose researches in this department of physics have earned him a lasting renown. He has given us an experimental demonstration of the kinetic theory of gases, and in his apparatus we can almost *see* the molecules as they fly about.

III. THE MOLECULAR THEORY OF LIQUIDS.

Preliminary Remarks. — I have already given you the kinetic definition of a liquid.* You will remember that liquids resemble gases in one respect, which is, that their molecules can move freely about among one another. They differ from gases, however, in having a much smaller average molecular velocity, and in having their molecules so close together that they are always well within the sphere of one another's attractive influence. Except when great accuracy is required, we found it possible to ignore the intermolecular forces in gases. This makes the molecular theory of these bodies comparatively simple. In liquids, however, no such simplification is possible, for the molecular forces are no longer insensible. Their effects are everywhere visible, and in discussing liquids we can never cease to consider them.

* Page 12.

This fact, and the more lamentable one that we do not yet certainly know the form of the molecular force-function (that is, the law of variation of the force with distance), render the study of liquids exceedingly difficult. Thus it is that although questions of the greatest moment are arising continually in this field of molecular physics, to most of them we can make no answer at present. No mathematician has yet worked out the kinetic theory of liquids to anything like the extent to which the corresponding theory of gases has been pushed; and for this reason what I shall say about liquids will necessarily be of a fragmentary character.

Free Evaporation. — There can be no doubt that the molecules composing liquids have as great a variety of velocities as those in gases; for there must be almost innumerable collisions among them, and even if there were an absolute equality of velocities at any given instant, the collisions would necessarily destroy this equality at once. Doubtless there is some law of distribution of velocities in liquids, corresponding to Maxwell's law in gases;* but the form of this law has not yet been discovered. Admitting the fact that the velocities of the molecules are unequal, let us consider what would happen at a free surface of the liquid, assuming for the moment that above this free surface there is a boundless vacuum. A particle well within the liquid is attracted, on the whole, equally in all directions. A particle at the *surface*, however, is attracted only *downward.* You will see, therefore, that when a molecule, in the course of its wanderings, comes to the surface, whether it will escape from the liquid or not depends upon the magnitude of the vertical component of its motion. If this vertical component is sufficient to carry the molecule beyond the range of sensible attraction of the liquid, the molecule will pass away indefinitely into the space above. On the other hand, if the vertical component of its motion is *not* sufficient to carry the mole-

* See equation (1).

cule beyond the range of sensible attraction of the liquid, it will rise into the vacuous space only a short distance, its upward velocity growing less and less under the influence of the downward attractive forces until it vanishes altogether, after which the molecule will begin to fall back again, and it will finally plunge once more into the liquid. At the surface of a liquid, therefore, the molecules are continually describing paths something like those indicated in this diagram (Fig. 27), where the dotted line represents the limit of sen-

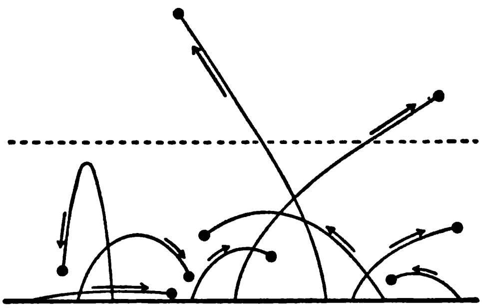


FIG. 27. — DIAGRAM OF A LIQUID SURFACE.

sible molecular attraction. Most of the molecules that start upward, fall back into the liquid; and the escape of such of them as are moving fast enough to overcome the attraction of the liquid, constitutes the phenomenon that we call *free evaporation.* I said that of those molecules that leave the liquid, the majority fall back again; and perhaps I ought to explain how we know this to be the fact. If the converse were true — that is, if the majority of them at once flew off into space — we should have to conclude that the average molecular velocity in liquids is just about great enough to overcome the attraction of the liquid for a molecule about to leave it; and the enormous latent heat of vaporization of liquids proves that this cannot be so. For example, we have to add a vast amount of energy to a pound of water before it will pass into steam; and this shows that under ordinary circumstances the

average kinetic energy of translation of a water-molecule is far too small to overcome the molecular attractive forces. Hence it follows that of the many molecules that come to the surface of a liquid in a given time, very few will permanently escape, because very few have velocities sufficiently in excess of the average to enable them to pass away, directly against the attractive force of the liquid.

Cooling Effect of Evaporation. — We know that the temperature of a gas is proportional to the average kinetic energy of translation of the molecules of the gas. It is not so certain that this is the case with *liquids*, for these bodies are constituted so differently that we can hardly assume them to act on our senses in precisely the same manner. Nevertheless, it is probable that there is some *analogous* relation between the kinetic energy of a liquid and the temperature of the liquid; so that although the two may not be strictly proportional, we may fairly assume, I think, that one of them is what mathematicians would call a continuous, one-valued, increasing function of the other. This being admitted, it is easy to see why evaporation cools a liquid. For it is plain that when a liquid is evaporating, it loses only those molecules which have a speed considerably greater than the average, — the slower moving ones, as I have explained, being retained by the attraction of the liquid. This is equivalent to saying that the molecules that *do* fly off will carry away with them more than their equable share of the kinetic energy of the liquid. Hence while evaporation is going on, the average kinetic energy per molecule, in the mother liquid, is continually growing less; and this means that the temperature of the liquid is falling.

Vapor Density. — Thus far we have spoken only of the phenomena of evaporation in a boundless vacuum, and we now come to the consideration of evaporation in a closed vessel. We will suppose that at the outset this vessel is

absolutely empty, and that at a certain instant a small quantity of water is admitted to it. During the first instant following the introduction of the water, the phenomena are precisely the same as we have seen them to be in the case of the boundless vacuum. The swiftest molecules fly off as before; but they can no longer pass away indefinitely into space. They are now retained by the vessel, in which they will accumulate, constituting a gas or vapor whose density will go on increasing until a certain limit is reached. You will readily see that the molecules composing this vapor will travel in every direction, precisely as they do in other gaseous bodies. Many of them, therefore, will plunge back into the liquid again, and become an integral part of it once more. Now the number of molecules that *leave* the mother liquid in a given time will be quite independent of the density of the vapor overhead; but the number that fly back into it again, in a given time, will be greater, the greater the density of the vapor. At the beginning of the evaporation the vapor will be rare, and the number of molecules that fly off in any given time will greatly exceed the number that return during that time. The density of the vapor will therefore increase. After a certain interval (an exceedingly *short* interval, measured by ordinary standards), the density of the vapor will become so great that the number of molecules plunging back into the liquid in a given time will become sensibly equal to the number that fly off from it in the same time. When this adjustment becomes perfect, the density of the vapor will no longer increase. It is then said to be "saturated." I would like to fix it clearly in your minds that a saturated vapor is one in which the number of molecules that plunge back into the mother liquid in any given time, is precisely equal to the number of molecules that rise out of the liquid, in the same time, and enter the vapor. You will see that any cause that tends to disturb this equality will also tend to alter the density of the vapor. For example, if we raise the temperature of the system we shall destroy the equality in question;

for we shall accelerate all the molecules, and hence more molecules will plunge from the vapor into the liquid in a given time than before, and more molecules will also come to the surface of the liquid from the interior. Furthermore, of the increased number of molecules that emerge from the interior of the liquid, a *larger proportion* than before will have velocities exceeding the critical velocity that a molecule must have in order to escape from the attraction of its fellows. Hence, on the whole, the density of the vapor will increase, approaching a new limit at which the number of in-coming and out-going molecules will again become equal. We see, therefore, that for any given vapor in contact with its liquid there is a definite density corresponding to each temperature. If we knew enough about the physics of liquids and vapors, we could express the relation between temperature and vapor density by means of a rational equation; but unfortunately we are still very far indeed from possessing this knowledge. Our reasoning shows that the density of a saturated vapor in no wise depends upon the size or shape of the containing vessel; and this is known to be the fact. It is also independent of the area of the free surface of the liquid, though this, perhaps, may not be so evident. If the free surface be doubled (for example), we shall thereby double the number of both the out-going and the in-coming molecules; hence the equality between the two will not be disturbed, and this shows that the vapor density does not depend upon the extent of the free surface of the liquid.

Vapor Pressure. — The pressure exerted by a vapor depends (1) on the average speed of the molecules composing the vapor, and (2) on the number of these molecules that strike against a unit area of the containing vessel, per second. The number of molecules that strike against a given area in a given time will depend on the number of molecules in a unit volume of the vapor — that is, on the *density* of the vapor — and on the average molecular velocity. Hence (since the average molec-

ular velocity is a function of the *temperature*) we may say that the pressure exerted by a vapor on the walls of the containing vessel will depend on (1) the density of the vapor, and (2) its temperature. This much is true of all gaseous bodies, as I have already explained to you while speaking of gases; but in the case of a saturated vapor in contact with its liquid, we have just seen that the density of the vapor is itself a function of the temperature. Hence we conclude that the pressure exerted by such a vapor against the vessel containing it depends, ultimately, only upon the temperature of the vapor and its liquid. This fact has long been known from experiment, and many attempts have been made to find an equation which should represent the relation between the pressure and temperature of saturated vapors. Of the many equations that have been proposed, Rankine's is probably as good as any. He found that the relation in question could be represented with remarkable accuracy by an equation of the form

$$\log p = \alpha - \frac{\beta}{t} - \frac{\gamma}{t^2}$$

where p is the pressure, t the absolute temperature, and α, β, and γ are constant quantities, to be determined for each liquid by experiment.*

Ebullition. — Although we saw that the density of a saturated vapor is not, strictly speaking, a function of the area of the free surface of the liquid, it must nevertheless be borne in mind that the process of evaporation is of such a nature that it cannot take place unless there is *some* free surface. For it consists in the escape of certain molecules from a free surface; and where there is no such surface, obviously there can be no evaporation. It is not essential that the free surface should be at the *top* of the liquid. For example, when

* For the values of α, β, and γ for various liquids, see Rankine's *Miscellaneous Scientific Papers* (London, Charles Griffin & Company, 1881).

water is heated, the air that it holds in solution is deposited in small bubbles on the walls of the containing vessel; and evaporation may take place across the surface of these bubbles, the bubbles increasing in size as they fill with steam, until presently they rise to the surface and break. If water be freed from such dissolved air, by protracted boiling or otherwise, it may be made to behave in a remarkable manner. Thus Dufour found that if drops of water so prepared are submerged in a mixture of oil of cloves and linseed oil (of specific gravity 1.000), they can be heated far above the boiling point, although exposed only to atmospheric pressure. Such drops have no free surface, and therefore no evaporation can take place from them. Dufour heated large drops of water, in this way, up to 248° Fahr., and he succeeded in heating smaller ones as high as 352° Fahr. (Under ordinary circumstances water could not be heated to 352° unless it were subjected to a pressure of at least 139 pounds, absolute, to the square inch.) When these drops came in contact with the thermometer, or with the containing vessel, they passed instantly into steam, with a hissing sound. It seems probable that the explanation of such phenomena as these is, that when the liquid is heated gradually and uniformly, without any free surface, its molecules are accelerated throughout the mass, but in such a uniform manner that the momentum is nowhere sufficient to tear them apart against the attractive forces that exist among them. When the velocities become so great that in parts of the drop they are on the point of tearing the molecules apart, the least disturbance from without, such as a shock or a vibration or the contact of some foreign substance, may precipitate the disruption; and after a free surface has once been formed, even though it may be exceedingly small, the drop will be almost instantly dissipated by evaporation across this surface. Ebullition differs from simple evaporation in the formation of such free surfaces in the interior of the liquid, or along the bottom and sides of the containing vessel, across which surfaces evaporation occurs

precisely as we have described it in connection with the upper, horizontal surface, or in connection with the air-bubbles separated from solution by heat. Ebullition appears to occur only when heat is supplied to the liquid faster than it can diffuse to the surface layers, or be carried there by convection. The cause of the formation of free surfaces in the interior of a boiling liquid is not well understood yet, and in fact it may be said, in general, that we have still much to learn concerning the phenomena of ebullition, both by the making of new experiments, and by interpreting those that have been made already.*

Critical Points. — Before leaving the subject of vapors and evaporation, I want to call your attention to a peculiar fact which was discovered experimentally, I believe, before it was explained theoretically; though its theoretical explanation is quite simple. I refer to the fact that there is a temperature for every gas — called its *critical* temperature — such that the gas cannot be liquefied by pressure alone when its temperature exceeds this critical value, no matter how great the applied pressure may be. In speaking of the theory of evaporation, I called your attention to the fact that a molecule cannot leave its liquid unless its upward velocity exceeds a certain limit. Now if molecules attract one another, there must be a similar proposition true of *molecules that collide with one another* in a vapor or a gas. Let me illustrate. A stone thrown upward by the hand does not travel far before the attractive force of the earth upon it overcomes its momentum, and causes it to fall back again. By using a rifle we can project a ball far higher into the air, but still it is only a matter of time when the momentum will be overcome, and the ball will fall back again just as the stone did. With a good modern *cannon* we can throw a projectile several miles

* In connection with this point, the reader is recommended to consult the section on "Evaporation and Ebullition" in Preston's *Theory of Heat* (Macmillan & Co., 1894).

into the air, — and still it falls back. But it is conceivable that we might project one with such speed that it would leave the earth forever. Such a result could be realized without giving the projectile an infinite velocity. I have no doubt that Professor Alden will show you, or has shown you, in your course in mechanics, that if the retarding action of the air be omitted from consideration, an initial speed of 36,650 feet per second would be quite sufficient. Now, with this much premised, let us imagine two molecules of a gas in contact; and let us suppose that a sudden impulse is given to one of them, to drive it away from the other. If the impulse is small enough, the disturbed molecule will only travel a short distance, and will then fall back to its original position; but we may give it such a speed that the attractive force of the fixed molecule will fail to bring it back, and in this case it will travel onward indefinitely. Now, just as in the case of the cannon-ball and the earth, there must be some intermediate velocity that will be *just sufficient* to separate the two molecules under consideration. We may call this the *critical velocity;* and we may say, that if the molecules of a gas are moving about so that, on an average, when two of them collide they have a relative velocity greater than this critical value, the gas in question cannot be liquefied by pressure alone; for even if its molecules were forced almost into absolute contact with one another, their velocities would be sufficient to separate them again indefinitely, as soon as the pressure was removed. From this, and from the relation between temperature and molecular velocity in gases, it follows that for every gas there is a *temperature* above which the gas cannot be liquefied. The critical temperatures of the so-called permanent gases are very low; and that is why they resisted liquefaction until the condition necessary to success in the experiment became known. The following table gives the critical temperatures of certain of the more familiar gases and liquids:

TABLE OF CRITICAL TEMPERATURES.

SUBSTANCE.	CHEMICAL FORMULA.	CRITICAL TEMPERATURE.	
		Centigrade.	Fahrenheit.
Hydrogen *	H	− 229°	− 380°
Nitrogen	N	− 124	− 191
Oxygen	O	− 118	− 180
Marsh gas	CH_4	− 100 (?)	− 148 (?)
Carbonic acid	CO_2	+ 31	+ 88
Nitrous oxide	N_2O	+ 36	+ 97
Ammonia gas	NH_3	+ 131	+ 268
Chlorine	Cl	+ 141	+ 286
Sulphur dioxide	SO_2	+ 156	+ 313
Ether	$(C_2H_5)_2O$	+ 194	+ 381
Alcohol	C_2H_6O	+ 235	+ 455
Chloroform	$CHCl_3$	+ 260	+ 500
Carbon disulphide	CS_2	+ 272	+ 522
Benzene	C_6H_6	+ 281	+ 538
Acetic acid	$C_2H_4O_2$	+ 322	+ 612
Water	H_2O	+ 365	+ 689

Contraction and Compressibility. — The well-known resistance of liquids to compression might seem to indicate that the molecules of these bodies are nearly in contact with one another; and the assumption that they are in contact has sometimes been made, for the purpose of deducing their diameters in accordance with a theorem of Clausius, to which I shall presently refer. The fact that liquids contract when cooled indicates, on the other hand, that their molecules are *not* in contact. I think I can tell you how these two things are to be reconciled. I think the difficulty of compressing liquids arises from the fact that their molecules are describing *curved paths* † with considerable velocities. They would fly off tangentially to these paths if it

* Calculated by Mr. Sutherland.

† See Fig. 10.

were not for the inter-molecular attractive forces that determine the curvature. Normally, therefore, there is a sort of balance between the attractive forces and the centrifugal tendency due to the velocity of the molecules and to the curvature of their paths. The centrifugal tendency developed by liquid molecules may be quite considerable, because it is proportional to the square of the velocity of translation, and to the *reciprocal* of the radius of curvature of the path. The radius of curvature of the path must be exceedingly small, because it is probably of the same order of magnitude as the distances between the molecules. Its reciprocal, therefore, will be correspondingly large, and hence the liquid molecules may have a considerable centrifugal tendency, even though their velocity of translation may be far less than it is in gases. Under normal conditions, as I have said, the attractive forces and the inertia effects are balanced, and the liquid remains at a constant volume. When we *cool* the liquid we diminish its kinetic energy — that is, we make its molecules go slower. This lessens the centrifugal tendency, the attractive forces preponderate, and the molecules approach one another; that is, the liquid *contracts*. When, instead of cooling the liquid, we compress it, the phenomena are not so simple. In reducing the bulk by compression we cause the molecules to approach one another. This lessens their potential energy, and therefore increases their kinetic energy; hence compression increases the average molecular speed. If all the other circumstances of the molecular motion remained the same as before, this increase of speed would increase the centrifugal tendencies of the molecules, and cause the liquid to resist compression. But in compressing a liquid we do not simply accelerate its molecules. In bringing them nearer one another we increase the attractive forces between them, and we undoubtedly alter the radii of curvature of their paths; and to predict the actual behavior of the liquid we should have to take all these things into consideration. The mathematical treatment of this problem is quite difficult, and

I cannot positively say what result it would yield. Nevertheless I am satisfied, in my own mind, that in forcing the molecules of a liquid closer together we increase the inertia effects far more than we increase the attractive forces, and that that is why liquids resist compression so powerfully.

Surface Tension. — The existence of molecular forces in liquids may be readily shown by experiment, and some of the experiments that have been devised for this purpose are exceedingly beautiful and suggestive; but before describing any of them I wish to call your attention to a fact which enables us to discuss molecular forces more conveniently than we otherwise could. Consider, for a moment, a drop of liquid, of which this (Fig. 28) is an imaginary sectional view. Particles in the interior of the liquid are attracted equally in every direction; but particles on the surface are attracted only *inward,* in a direction perpendicular to the surface of the drop. If we write the mathematical equations that would represent the behavior of a drop when acted upon by forces of this kind, we shall find that these equations are precisely the same as they would be in a similar drop whose parts do not attract one another, but which is enveloped by a water-tight skin, or membrane, *in a state of uniform tension.* The tension that such an imaginary membrane would have to have, to produce the observed phenomena of drops and other small portions of liquid, is called the *surface tension* of the liquid. It should be carefully noted that we do not assert that any such membrane *actually exists.* "Surface tension" is only a convenient conception that enables us to foresee, more clearly, the effects produced under given conditions by the molecular forces existing in liquid masses. I think I need not discuss

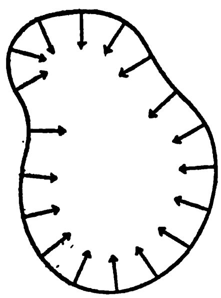


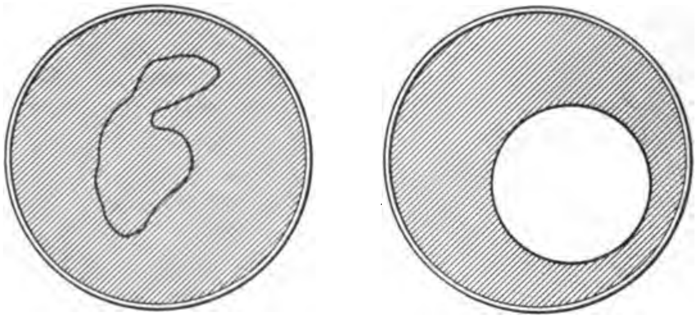
FIG. 28. — DIAGRAM ILLUSTRATING SURFACE FORCES IN A DROP OF LIQUID.

this conception further, because it is explained and illustrated in all good works on physics. It may be well, however, to call attention to the fact that the ideal surface membrane of liquids differs from all material membranes inasmuch as its tension does not increase when the surface of the liquid is extended in any way. When the surface of a liquid increases, it does so by the exposure of particles that were previously in the interior, and *not* by the stretching of the old surface, in the sense in which the word "stretch" is ordinarily used. This point seems obvious enough, but I find that unless particular attention is called to it, students are apt to get erroneous ideas about surface tension.

Phenomena of Films.—Regarding liquids as mobile bodies enclosed in contractile membranes in a state of uniform tension, it will be plain, I think, that the most notable effects of molecular attraction will be observed when the mass of the liquid is small in proportion to the surface it exposes. Thus the phenomena of soap-bubbles, and of other forms of liquid films, are very striking. A simple and beautiful experiment illustrating surface tension can be performed with a piece of wire, a bit of sewing silk, and a solution of soap, suitable for blowing bubbles.* The wire is bent into a ring, about 2½ inches in diameter, and a soap film is formed across it by simply immersing it in the soap solution and withdrawing it again. To make the film adhere, it may be necessary to roughen the ring with a file. A piece of sewing silk, about three inches long, is tied together at the ends, so as to form a closed loop. The silk loop is then wetted with the soap solution, and laid gently on the film. (See Fig. 29.) It will lie indifferently in any position if the film be kept perfectly horizontal, its indifference being due to the fact that the forces acting on it are balanced in all directions. If the film be broken *inside the silk loop*, by the contact of a dry

* Plateau's *liquide glycérique* is the best thing for blowing bubbles. See Appendix.

bit of wood or a hot needle, the loop instantly flies out into a perfect circle (Fig. 30), demonstrating the existence of the "surface tension" in a most interesting manner. (The same



FIGS. 29 and 30.—ILLUSTRATING THE SILK-LOOP EXPERIMENT.

experiment may be performed with the ring and film vertical, if the silk loop be supported as shown in Fig. 31.) When the circular silk ring is floating on the soap film, it is instructive to tap it lightly on the inside with a lead-pencil or other convenient small article. It springs away from the touch of the pencil as though it were a ring of tempered steel escaping from the blow of a hammer. This is because the tap with the pencil deforms it slightly, and the tension of the film immediately restoring it to the circular form causes it to react against the pencil very smartly, and to bound away from it with surprising quickness. An endless variety of beautiful experiments can be tried with soap films with extremely simple apparatus; but we cannot dwell upon them longer this evening. The one experiment that

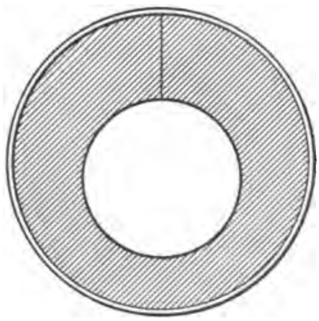


FIG. 31.—MODIFICATION OF THE SILK-LOOP EXPERIMENT.

I have described will be sufficient to show the existence of the molecular forces satisfactorily.

Other Surface Phenomena. — The surface tension of a liquid may be altered by a variety of methods. Thus if a small sliver of cork be carefully wetted with alcohol along half of its length *on one side*, and be then thrown upon water, it will revolve, because the surface tension of dilute alcohol is less than the surface tension of pure water, and the cork is

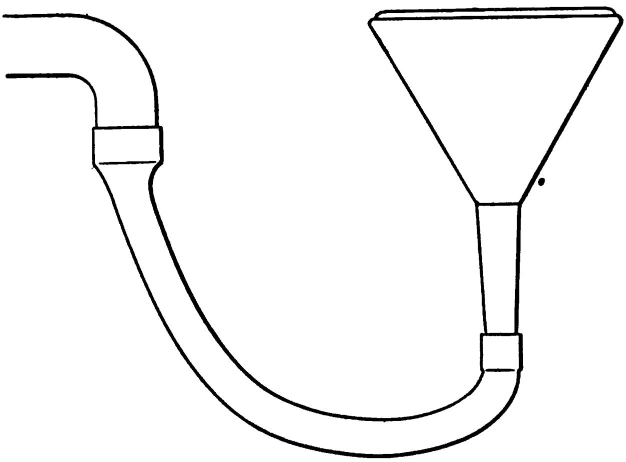


FIG. 32. — A METHOD FOR OBTAINING A CLEAN WATER-SURFACE.

therefore pulled more in one direction than the other. If a similar fragment of cork be wetted with alcohol or ether along one entire end or side, and thrown upon water, it will be pulled across the surface of the water bodily, for the same reason. Particles floating on the surface of clean water appear to be repelled by a drop of alcohol or ether, brought near to them on the end of a glass rod or the tip of a finger. This is because some of the vapor of the alcohol or ether condenses on the surface of the water and alters its tension in the vicinity of the drop. Small particles of camphor floating

on clean water exhibit vigorous movements. Camphor is slightly soluble in water, and its solution has a lower surface tension than pure water. The camphor particles do not dissolve with equal rapidity on all sides, and hence there is a resultant pull exerted on them, in the direction in which the water contains the least camphor in solution. For success in this experiment it is essential to have a perfectly *clean* water surface, as the least trace of oily matter deadens the movements remarkably. A good way to secure such a surface is shown in Fig. 32. An inverted glass funnel is connected with the faucet by a rubber tube, and the water is allowed to run freely for some time. The faucet is then turned off until only the least possible amount of water comes through it. A piece of camphor is next scraped clean, and a few of the last scrapings are allowed to fall on the water in the funnel. If the funnel was originally clean, they will spin about in a lively manner. We shall have occasion to refer to this experiment again, when we come to consider the size of molecules.

Magnitude of the Surface Tension.—If we could find out what the strain is on the silk thread shown in Fig. 30, we could calculate the intensity of the surface tension by the same formula that is used for calculating the bursting pressure of thin, hollow cylinders. It would be possible to devise an experiment that would give this strain, but it would hardly be worth while, because the surface tension of liquids can be determined by other methods more conveniently and with far greater accuracy. In fact, it can be determined directly, by means of an apparatus like that shown in Fig. 33, where S is a soap film, and W is a light wire, which can move up and down without sensible friction. By putting small weights in the pan we can readily discover what the supporting power of the film is. This result is to be divided by the length of that part of the wire W which is wetted by the film, and the quotient is the supporting power of the film, per unit length

of *W*. To find the surface tension we have to divide the supporting power thus found by 2, because the film has two surfaces. Experiments of this sort are interesting enough, but they are of small value, because they can only give us the surface tension of *soap solutions*, or of other liquids from which bubbles can be blown. Different methods have to be used, therefore, to determine the surface tension of pure water and the great majority of liquids. Many such methods have been proposed. One of them is based on the investigation of the curved surface of a liquid, where it touches the vessel containing it. You are all familiar with the appearance of the water curve, and I think you would be ready to admit that the experimental investigation of its shape would

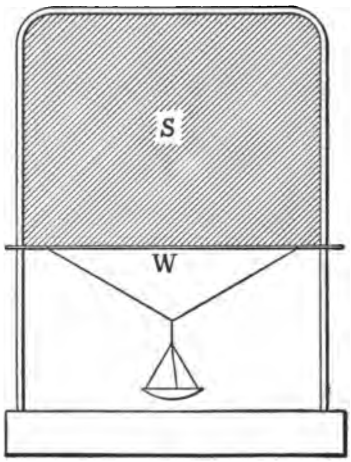


FIG. 33.—APPARATUS FOR MEASURING SURFACE TENSION.

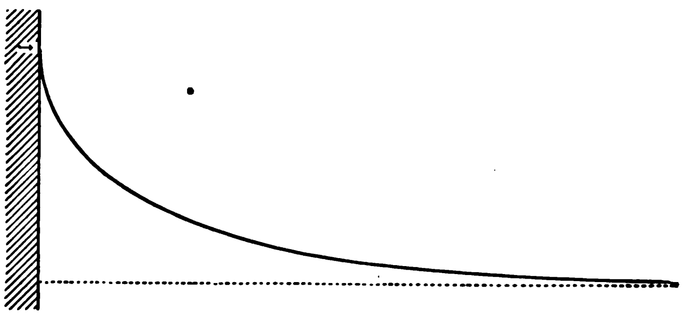


FIG. 34.—THE WATER CURVE; FROM HAGEN'S MEASURES.

be very difficult. The difficulties have been overcome, however, by numerous observers; and I have plotted for you,

from Hagen's data, the form assumed by a water surface in the vicinity of a flat, vertical plate of polished brass (Fig. 34).* The dotted line shows the level of the water at an infinite distance from the plate, it being an asymptote to the water-curve. It can easily be shown that if y is the height, above the dotted line, of any point, P, on the water-curve, and a is the angle that the tangent at P makes with the dotted line, then

$$y=2\sqrt{\frac{S}{w}}.\ \sin\frac{a}{2}, \tag{35}$$

where S is the pull exerted by the water surface on a line one unit long, and w is the weight of a unit volume of water. This equation is derived from the fact that the curvature of the surface at any point must be just sufficient to enable the superficial tension to support a column of water of height y. You will see that if we measure a and y at any point, and substitute their values in the equation I have just given, we can calculate S (w being a known quantity). The principal objection to this method is the difficulty of determining the coördinates of the water-curve accurately. A very simple method of finding the surface tension consists in observing the height, h, to which a liquid will rise in a capillary tube of radius r. The surface tension, S, is then given by the equation †

$$S=\frac{w\,r\,h}{2\cos a},$$

where w is the weight of a unit volume of the liquid, and a is the angle which the surface of the liquid makes with the tube at the point where the two come into actual contact. With a clean glass tube the value of a for water is 0°, and for mercury it is 128° 52′. The capillary-tube method gives

* The scale of Fig. 34 is such, that every dimension in the cut is ten times the corresponding dimension in nature.

† For the derivation of this equation see Maxwell's article on *Capillary Action* in the *Encyclopædia Britannica.*

fairly satisfactory results, but the angle a varies considerably with the degree of cleanliness of the surface of the glass tube, and it would be desirable to have a good method that would be free from any such objection. I believe that Lord Kelvin's method meets every requirement in this respect, and although I have not tried it, and do not know what results

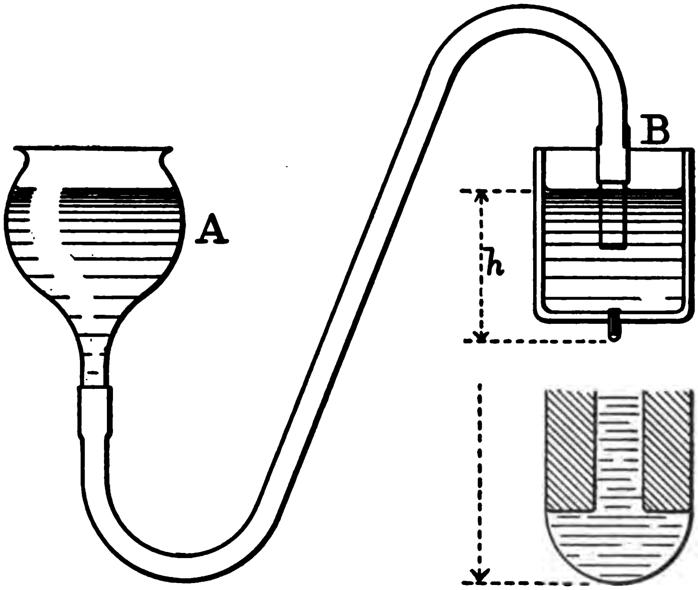


FIG. 35.—LORD KELVIN'S APPARATUS FOR DETERMINING SURFACE TENSION.

FIG. 36.—NOZZLE OF LORD KELVIN'S APPARATUS.

have been obtained from it by others, I am going to tell you, briefly, what his plan is.* His apparatus consists of two vessels, A and B (Fig. 35), connected by a flexible syphon in such a manner that the level of the liquid in B can be varied at will by raising or lowering A. At the bottom of B there is a small nozzle with a capillary opening through it (shown on an enlarged scale in Fig. 36). The liquid in B runs down

* See his *Popular Lectures and Addresses*, Vol. I, p. 45.

through the nozzle, and if the height h is not too great, a drop will form at the bottom of the nozzle, whose radius of curvature will be just sufficient to enable the surface tension at that point to sustain a column of liquid of height h. This radius of curvature is next determined by any of the methods given in the books on physics that are applicable to the case — some optical method being preferable — and the surface tension is then given by the equation

$$S=\frac{pr}{2}=\frac{whr}{2} \tag{36}$$

where r is the radius of curvature of the drop, and w is the weight of a unit volume of the liquid. In his article on *Capillary Action* in the *Encyclopædia Britannica*, Maxwell gives the following values of the surface tensions of various liquids at 20° C. (68° Fahr.), as determined by Quincke, the

TABLE OF SURFACE TENSIONS AT 20° C.

Liquid.	Surface Tension.			
	Specific Gravity.	Dynes per Centimeter.	Grammes per Centimeter.	Grains per Inch.
Water	1.0000	81	.083	3.24
Mercury	13.5432	540	.551	21.58
Bisulphide of carbon .	1.2687	32.1	.033	1.28
Chloroform	1.4878	30.6	.031	1.22
Alcohol	0.7906	25.5	.026	1.02
Olive oil	0.9136	36.9	.038	1.47
Turpentine	0.8867	29.7	.030	1.19
Petroleum	0.7977	31.7	.032	1.27
Hydrochloric acid . .	1.1	70.1	.071	2.80
Solution of hyposulphite of sodium	1.1248	77.5	.079	3.10

free surface of the liquid being in contact with air in every case. He gives the tensions as expressed in dynes per linear centimeter, and I have reduced them also to grammes per linear centimeter and to grains per linear inch; so that the last column gives the normal pull, in grains, exerted by a liquid on a straight line, one inch long, lying in its surface. (Of course there is an equal and opposite pull on the other side of the line, unless it happens to form one of the boundaries of the surface, as shown at W in Fig. 33.)

The value of the surface tension of water given in this table is certainly too great. Brunner found it to be 75.2 dynes, and Wolf found 76.5 and 77.3. Rayleigh's determination, based on a study of the wave-length of ripples, gave 73.9 dynes at 18° C. The latest trustworthy determination that I have seen is that given by Mr. T. Proctor Hall in the *Philosophical Magazine* for November, 1893. He finds that at $t°$ centigrade the surface tension of water, in dynes per linear centimeter, is $75.48 - .140\ t$, which is equivalent to $.07694 - .000143\ t$ when expressed in grammes per linear centimeter.

Latent Heat of Vaporization. — To vaporize a given mass of liquid we have to tear all its molecules apart, in opposition to the attractive forces that exist among them, and we have also to increase the average speed of the molecules. Each of these operations necessitates the expenditure of energy, and the total amount of energy thus required is surprisingly large. For example, to vaporize one pound of water (about a pint) at 212° Fahr., we have to expend no less than 966 British units of heat, or about 753,000 foot-pounds of energy. This shows that although the range of sensible molecular attraction, in water and other liquids, is quite small, the attractive forces, where they exist, must be very great. Following are the latent heats of vaporization of a few familiar liquids.

LATENT HEATS OF VAPORIZATION.*

Liquid.	Latent Heat.	
	Heat Units.	Centimeter-Kilograms.
Water	535.9	22,883
Alcohol	202.4	8,642
Bisulphide of Carbon . . .	86.7	3,702
Mercury	62.0	2,647

Investigation of the Work done in bringing a Molecule to the Surface. — A molecule in the interior of a liquid is always under the influence of the attractive forces of its neighbors, and the resultant force exerted upon it at any instant must be found by compounding the attractions of all the molecules that are near enough to have any sensible effect upon it. The ceaseless change of position that goes on among the molecules of a liquid causes this resultant force to assume all imaginable directions and magnitudes in rapid succession; and it follows that the molecule under consideration is in a sort of *statistical equilibrium,* if I may use the phrase. This is the kind of equilibrium that is contemplated when we say that molecules in the interior of a liquid are attracted equally in every direction. With this much premised I am going to tell you of a property of liquids that we shall use, presently, in estimating the sizes of molecules. The property that I refer to is this: Whatever the law of molecular attraction may be, the work that has to be done *against molecular attractive forces* in bringing a particle of a liquid from the interior to the surface is precisely one half of the work that would have to be done to transport that particle from the interior of the liquid to an infinite distance. In proving this proposition we shall con-

* At the boiling points of the respective liquids. A gramme of the liquid is considered in each case, and the unit of heat is the heat required to raise the temperature of one gramme of water from 3° C. to 4° C.

ceive a sphere to be described about the particle as a center, the radius of the sphere (which we will denote by R) being such that the attractions of all the particles that lie outside of it can be neglected. So long as the sphere is wholly submerged, the particle is in equilibrium; but when the distance of the particle from the surface of the liquid becomes less than R, a portion of the sphere will project above the liquid, and the particle will no longer be in equilibrium, but will be attracted downward, towards the interior. For example, consider this diagram (Fig. 37), the upper part of which illus-

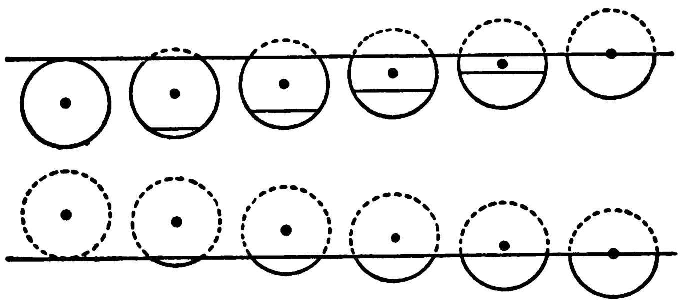


FIG. 37.—DIAGRAM TO ILLUSTRATE THE WORK DONE IN BRINGING A PARTICLE OF LIQUID TO THE SURFACE.

trates six successive stages of the approach of the particle to the surface. In the first stage, shown on the left, the sphere just touches the surface. In the next stage a part of the sphere projects above the liquid, and therefore there is a resultant downward attraction on the particle. To find the magnitude of this resultant, conceive a horizontal plane to be passed through the lower part of the sphere so as to cut off a segment equal to that which projects above the surface of the liquid. (The plane in question is indicated in the diagram by a short, straight line.) It follows from the symmetry of the figure that the component attractions of all the molecules that lie above this plane are perfectly balanced; and hence the resultant attraction of the liquid on the particle we are considering is equal to the attraction exerted upon it by the

segment that the imaginary plane cuts off from the lower part of the sphere. You will see that the same reasoning applies at every stage, until the particle finally lies in the surface, as shown on the right. Now, if you please, turn your attention to the lower half of the diagram, which represents six corresponding stages in the removal of the particle from the surface of the liquid to an infinite distance. As we pass from right to left, the particle, in each position, is attracted downward by the segment of the sphere which lies within the liquid. By comparing the upper and lower parts of the diagram, you will see (1) that the particle is attracted *downward,* whether it is above the surface or below it; and (2) that the *magnitude* of the attraction is the same, when the particle is at a given distance from the surface, whether the particle is inside the liquid or outside. It follows from this symmetry of the attractions, that the work required to bring the particle to the surface of the liquid is precisely equal to the work required to carry it from the surface to a point outside where the attraction of the liquid is no longer sensible; and that is the same thing as saying that the work required to bring the particle to the surface is one half of the work required to transport it from the interior of the liquid to an infinite distance.

Numerical Estimation of the Work done in bringing a Molecule to the Surface. — We are now in position to compute the work that would have to be expended, against intermolecular forces, in bringing to the surface of any given liquid a small portion of it, of given weight, originally situated in the interior. For, let us consider what happens when a unit weight of the liquid, originally at (say) 20° C., is heated to its boiling point and then entirely evaporated. In the first place, the mass of liquid contains a certain quantity of *kinetic energy,* because its molecules are certainly in motion. We cannot calculate this energy, because we do not know enough about the velocities of molecules in liquids.

For the present, therefore, we shall merely denote it by k_1. We next proceed to raise the temperature of the liquid from 20° C. to the boiling point. In doing so we accelerate the molecules of the liquid, and (since the liquid expands upon being heated) we also do a certain amount of work in pulling the molecules apart, against the attractive forces they exert upon one another. The kinetic energy that has been added, in increasing the speed of the molecules, will be denoted by k_2; and the total amount of heat-energy that we had to add in order to raise the temperature from 20° C. to the boiling point will be denoted by h. The next step is to evaporate the liquid; and in order to effect the evaporation we have to supply the quantity of heat known as the "latent heat of vaporization," which we shall represent by H. The unit weight of liquid has now been transformed into a unit weight of vapor, and obviously we have the relation

$$h + H = k_2 + k_3 + W + w, \qquad (37)$$

where k_2 is the kinetic energy added in heating the liquid from 20° C. to the boiling point, k_3 is the kinetic energy added in transforming the boiling-hot liquid into vapor, W is the total energy expended in overcoming molecular attractions, and w is the so-called "external latent heat" — that is, the work done by the vapor in expanding from the liquid-volume to the vapor-volume against atmospheric pressure. Of these quantities we know H, h, and w, and although we do not know k_2 and k_3 separately, we can compute their sum with a sufficient degree of approximation. In fact,

$$k_1 + k_2 + k_3 = K,$$

where K is the *total kinetic energy* of the vapor, which can be computed when we know the number of degrees of freedom of the molecules, and their average velocity of translation. We may observe that k_1 is the kinetic energy of the molecules in the liquid state; and since the kinetic energy of a

body varies as the *square* of the body's velocity, and we have good reason to believe that the molecular velocity in a liquid is far less than it is in the vapor of that liquid, it follows that k_1 is extremely small in comparison with K. We shall therefore neglect it, and consider $k_2 + k_3$ to be equal to K. With this modification (37) becomes equivalent to

$$W = H + h - K - w. \tag{38}$$

The quantities H and h are given in the books on heat, from which source data can also be had for computing w. To determine K we shall treat the vapor as a perfect gas; for although this mode of procedure is not strictly correct, it will give results accurate enough for our purpose. We have, as the kinetic energy *of translation* in a given mass of vapor,

$$k = \tfrac{1}{2} M u^2, \tag{39}$$

where M is the mass of the vapor and u^2 is the mean-square velocity of its molecules, as defined in equation (5). But we also have

$$p = \frac{u^2 \Delta}{3},^* \tag{40}$$

where Δ, being the absolute density of the vapor, is equal to its *mass* divided by its *volume* — that is,

$$\Delta = \frac{M}{V}.$$

Substituting this value of Δ in (40), we find that

$$M u^2 = 3 p V,$$

which, in (39), gives

$$k = \tfrac{3}{2} p V.$$

Now k, being the total kinetic energy *of translation* of the vapor, involves *three* degrees of freedom; and hence K, the *total* kinetic energy, is found by multiplying k by $\frac{n}{3}$, where n

* See equation (13).

is the number of degrees of freedom in the vapor under consideration. When n is not certainly known (as in most cases it is not), we shall be obliged to substitute for it its value in terms of γ, as given by equation (22). I am aware that grave objections could be urged against such a substitution in the case of vapors, but it is the best we can do. It gives us

$$K=\frac{n\,k}{3}=\frac{2\,k}{3\,(\gamma-1)}=\frac{p\,V}{\gamma-1}. \tag{41}$$

By computing K in accordance with this equation for the four liquids whose latent heats of vaporization are given on page 96, we obtain the values given in the fourth column of the accompanying table.

COMPUTATION OF THE WORK DONE AGAINST MOLECULAR ATTRACTION IN BRINGING A GRAMME OF LIQUID TO THE SURFACE, AT 20° C.

LIQUID	H	h	K	w	W	$\frac{1}{2}W$
Water	22,880	3,420	5,910	1,750	18,640	9,320
Alcohol	8,640	1,690	6,180	630	3,520	1,760
Bisulphide of Carbon .	3,700	290	1,790	350	1,850	925
Mercury	2,650	470	390	260	2,470	1,235

All of the quantities in the table are expressed in centimeter-kilograms, and, as the heading indicates, the computation is performed for one gramme of liquid in each case. The various quantities are given only approximately, and the results have the same order of certainty (or uncertainty) as the values of γ that I have used in equation (41). The quantity W is obtained by substituting H, h, K, and w in equation (38); and as W is the work that would have to be expended, against molecular attraction, in order to transport a gramme of the liquid from the interior of the liquid to an infinite distance (taking it away a molecule at a time), it follows, from the preceding section, that $\frac{1}{2}W$ is the work that we should have to do in order to bring to the surface a gramme

of liquid that was previously in the interior. I have dwelt upon this computation at greater length than its intrinsic importance would warrant, because, as I have already told you, we shall presently make use of it in determining the sizes of molecules.

IV. THE MOLECULAR THEORY OF SOLIDS.

Condition of the Theory. — The molecular theory of solids is still in its veriest infancy; in fact it might almost be said that there is no such theory. The phenomena exhibited by solids are extremely complicated, and this fact implies, without doubt, a corresponding complexity in molecular structure. In order to give you a clear idea of the formidable task that lies before the philosopher who would penetrate the inner secrets of the solid condition of matter, let me quote a few words from Maxwell. "The stress [in a solid body] at any given instant," he says, "depends not only on the strain at that instant, but on the previous history of the body. Thus the stress is somewhat greater when the strain is increasing than when it is diminishing, and if the strain is continued for a long time, the body, when left to itself, does not at once return to its original shape, but appears to have taken a set, which, however, is not a permanent set, for the body slowly creeps back towards its original shape with a motion which may be observed to go on for hours and even weeks after the body is left to itself. . . . The phenomena are most easily observed by twisting a fine wire suspended from a fixed support, and having a small mirror suspended from the lower end, the position of which can be observed in the usual way by means of a telescope and scale. If the lower end of the wire is turned round through an angle not too great, and then left to itself, the mirror makes oscillations, the extent of which may be read off on the scale. These oscillations decay much more rapidly than if the only retarding force were the resistance of the air, showing that the force of torsion in the

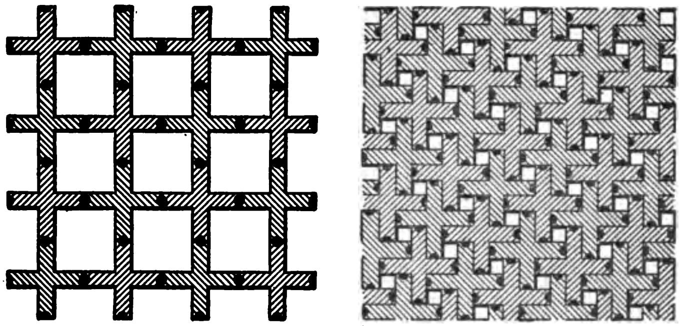
wire must be greater when the twist is increasing than when it is diminishing. This is the phenomenon described by Sir W. Thomson under the name of the viscosity of elastic solids. But we may also determine the middle point of these oscillations, or the point of temporary equilibrium when the oscillations have subsided, and trace the variations of its position. If we begin by keeping the wire twisted, say for a minute or an hour, and then leave it to itself, we find that the point of temporary equilibrium is displaced in the direction of twisting, and that this displacement is greater the longer the wire has been kept twisted. But this displacement of the point of equilibrium is not of the nature of a permanent set, for the wire, if left to itself, creeps back towards its original position, but always slower and slower. This slow motion has been observed by the writer going on for more than a week, and he has also found that if the wire were set in vibration the motion of the point of equilibrium was more rapid than when the wire was not in vibration. We may produce a very complicated series of motions of the lower end of the wire by previously subjecting the wire to a series of twists. For instance, we may first twist it in the positive direction, and keep it twisted for a day, then in the negative direction for an hour, and then in the positive direction for a minute. When the wire is left to itself the displacement, at first positive, becomes negative in a few seconds, and this negative displacement increases for some time. It then diminishes, and the displacement becomes positive, and lasts a longer time, till it, too, finally dies away."* I think I need not add anything to the passage I have just quoted. The facts to be explained by the molecular theory of solids are certainly forbidding enough, and it is not strange that so little progress has been made.

Arrangement of the Molecules in Solids.—The most obvious property of a solid is, that it preserves its shape so

* *Encyclopædia Britannica*, article *Constitution of Bodies.*

long as it is not acted upon by external forces. Moreover, when such forces *are* applied, the solid indeed becomes deformed, but it eventually regains its original shape after the forces have been removed, provided they did not exceed a certain magnitude called the "elastic limit," which is peculiar to the solid under examination and to the way in which the forces were applied. We are obliged to conclude, from these facts, that the molecules of a solid are not free to roam about, but that some or all of them have determinate mean positions about which they may oscillate and rotate, but from which they never permanently depart except when constrained to do so by an external force greater than whatever the forces may be that determine the mean positions. In order to gain a clearer insight into the nature of solids, let us now regard them from a somewhat different point of view — let us consider the transition of a liquid into a solid by congelation. It is well known that when a liquid is cooled to a certain point peculiar to itself, it solidifies, changing its volume at the same time and giving out a certain amount of heat, called the "latent heat of fusion." We are therefore impelled to believe that when the average kinetic energy of translation of the liquid molecules is reduced to a certain value by the abstraction of heat, the inter-molecular attractive forces become able to restrict the migrations of the molecules, and to confine them, as I have already said, to certain mean positions. Furthermore, since energy cannot be created or destroyed, the fact that the body gives up a certain amount of "latent heat" when it solidifies must necessarily imply that there has been a diminution in the kinetic energy of the molecules, or in their potential energy, or in both. Now there undoubtedly is some loss of kinetic energy when a liquid solidifies, but I think we can assert that there is a loss of potential energy also, just as there is when a gas condenses into a liquid. If all liquids contracted upon solidifying it would be plain that potential energy disappears during the process; for contraction would imply that the molecules

approach one another. The fact is, however, that many liquids *expand* upon solidification, water being a familiar example of this. Hence we are called upon to explain how it can be that the potential energy in a body can grow less when the molecules of the body go farther apart. I believe that this question has a close bearing on the *constitution* of molecules — a subject of which we know practically nothing, at present. If you will glance at these diagrams, however, (Figs. 38 and 39,) I think you will see that the condition of



FIGS. 38 and 39. — ILLUSTRATING MINIMUM POTENTIAL ENERGY AND MINIMUM VOLUME.

least potential energy in a system of bodies does not necessarily coincide with that of closest approach of the centers of those bodies. The diagrams are not intended to represent molecules in any sense, but they may serve to illustrate the point under consideration. I have assumed that each of these ideal bodies has four attractive *poles*, which are represented by the black spots. The centers of attraction, or *poles*, of such bodies would tend to approach one another as closely as possible, and the potential energy of the system would be least when the poles were nearest together — that is, when the arrangement was like that shown in Fig. 38. If the bodies were placed as shown in Fig. 39 the total volume would be least, but the potential energy in that case would be greater than in the arrangement shown in Fig. 38, because

the attractive poles are further apart. It is plain, therefore, that the potential energy of a system of bodies is not necessarily least when the space occupied by the system is least. In other words, the equipotential surfaces of molecules are not necessarily spherical. This conclusion, derived from a consideration of the phenomena of congelation, is confirmed by a study of the physical properties of crystals with unequal axes.

Maxwell's Views Concerning the Molecular Constitution of Solids. — In speaking of the classification of bodies under the three heads of solids, liquids, and gases, I said, in the early part of the evening, that such a division is not entirely satisfactory; and we have now come to a point where we must examine this classification more carefully. Many bodies are undoubtedly solids, and many others are undoubtedly liquids; but there are bodies, such as wax, pitch, and tar, which possess some of the properties of each, and which are quite difficult to classify satisfactorily. A mass of pitch, for example, may be brittle, so that it is easily shattered by a blow, and yet this same mass, when placed on an inclined plane, loses its shape and flows slowly down the plane. It may not reach the bottom for months, or perhaps years; but a true solid would remain where it was placed, for all eternity.* To account for the properties of pitch-like bodies, and for the peculiar behavior of wires and other solids when submitted to strains, Maxwell has proposed the following hypothesis: "We know that the molecules of all bodies are in motion. In gases and liquids the motion is such that there is nothing to prevent any molecule from passing from any part of the mass to any other part; but in solids we must suppose that *some*, at least, of the molecules merely oscillate about a certain mean position, so that, if we consider a certain group of molecules, its configuration is never very different

* It is assumed, of course, that the inclination of the plane is not great enough for either body to *slide* upon it.

from a certain stable configuration, about which it oscillates. This will be the case even when the solid is in a state of strain, provided the amplitude of the oscillations does not exceed a certain limit, but if it exceeds this limit the group does not tend to return to its former configuration, but begins to oscillate about a new configuration of stability, the strain in which is either zero, or at least less than in the original configuration. The condition of this breaking up of a configuration must depend partly on the amplitude of the oscillations, and partly on the amount of strain in the original configuration; and we may suppose that different groups of molecules, even in a homogeneous solid, are not in similar circumstances in this respect. Thus we may suppose that in a certain number of groups the ordinary agitation of the molecules is liable to accumulate so much that every now and then the configuration of one of the groups breaks up, and this whether it is in a state of strain or not. We may in this case assume that in every second a certain proportion of the groups break up, and assume configurations corresponding to a strain uniform in all directions. If all the groups were of this kind, the medium would be a viscous fluid. But we may suppose that there are other groups, the configuration of which is so stable that they will not break up under the ordinary agitation of the molecules unless the average strain exceeds a certain limit, and this limit may be different for different systems of these groups. Now if such groups of greater stability are disseminated through the substance in such abundance as to build up a solid framework, the substance will be a solid, which will not be permanently deformed except by a stress greater than a certain given stress. But if the solid also contains groups of smaller stability and also groups of the first kind which break up of themselves, then when a strain is applied the resistance to it will gradually diminish as the groups of the first kind break up, and this will go on till the stress is reduced to that due to the more permanent groups. If the body is now left to itself, it will

not at once return to its original form, but will only do so when the groups of the first kind have broken up so often as to get back to their original state of strain. This view of the constitution of a solid, as consisting of groups of molecules some of which are in different circumstances from others, also helps to explain the state of the solid after a permanent deformation has been given to it. In this case some of the less stable groups have broken up and assumed new configurations, but it is quite possible that others, more stable, may still retain their original configurations, so that the form of the body is determined by the equilibrium between these two sets of groups; but if, on account of rise of temperature, increase of moisture, violent vibration, or any other cause, the breaking up of the less stable groups is facilitated, the more stable groups may again assert their sway, and tend to restore the body to the shape it had before its deformation."* I have quoted Maxwell's words at length, both because he has stated his views with remarkable lucidity, and because his hypothesis, so far as I know, is the only one yet proposed that is at all adequate to explain the complicated phenomena exhibited by solid bodies. Even here we should proceed with caution, however, for the hypothesis that he offers us, profound and beautiful as it is, cannot logically be regarded as anything *more* than a hypothesis until its consequences have been worked out mathematically, and compared with the facts.

Sublimation.—Some solids exhibit a phenomenon quite analogous to evaporation, to which phenomenon the name of *sublimation* has been given. There are doubtless frequent collisions among the molecules of solids, precisely as there are among those of liquids and gases. Such being the case, we must conclude that the velocities of oscillation and rotation of the molecules of solids are not all equal; and doubtless there is also some undiscovered law of distribution of these

* *Encyclopædia Britannica*, article *Constitution of Bodies*.

velocities, analogous to Maxwell's law for gases. If this be admitted, we may infer that every now and then a molecule on the exterior of a solid will have an impetus sufficient to overcome the restraining forces, and to tear itself away and escape from the solid, just as molecules escape from a liquid in evaporation. With some solids, such as camphor, this action is very noticeable. Ice also evaporates (or sublimes), in dry air, at temperatures below the melting point. These two substances, as well as others, even have a definite vapor pressure corresponding to each temperature, just as liquids do when placed in closed vessels. The reason for this definite relation between temperature and vapor pressure need not be repeated, for it is precisely the same as I have already given you in speaking of evaporation from liquids. Many solids, such as iron and stone, do not sensibly sublime at any temperature, though metals and argillaceous earths and other non-volatile solids often have characteristic odors which may possibly be due to a slight loss of substance by sublimation. Other solids, such as arsenic, sublime freely at elevated temperatures, mercury bichloride, or "corrosive sublimate," taking its popular name from this property. There are reasons for believing that even carbon is slightly volatile at high temperatures — at least under the conditions to which it is exposed in the bulbs of incandescent electric lamps. It must be admitted that solids, in general, do not sublime as freely as one might naturally expect them to; and the reason for this probably is, that the intermolecular forces in these bodies are so enormous that it is seldom that a molecule happens to have a velocity great enough to enable it to fly away. (That the attractive forces between neighboring molecules are great, in solids, is shown by the tensile strength of these bodies.) When the intermolecular forces in solids are counterbalanced in some degree by other forces, acting in opposition to them, there is often a loss of molecules from the solid, and the resulting phenomena correspond, to some extent, with those of sublimation. Examples of this are afforded by the phenom-

enon known as *solution*, and also by that known as *dissociation*. We shall consider dissociation first.

Dissociation. — If steam be passed through a tube containing red-hot iron-filings, the steam is decomposed, black oxide of iron is formed, and hydrogen escapes from the free end of the tube. On the other hand, if hydrogen be passed through a red-hot tube containing black oxide of iron, the oxide is reduced to metallic iron, the liberated oxygen combines with the hydrogen, and steam escapes from the free end of the tube. These apparently contradictory phenomena were first adequately explained by Deville ; and in order to understand his explanation properly, let us first consider what forces are involved in the problem. (1) The hydrogen molecule being double, we have to consider the attraction of its two component atoms for each other. (2) We have likewise to consider the attraction that the atoms composing an iron molecule exert upon one another, and also (3) the attractions existing among the atoms of a steam molecule, and (4) those existing among the atoms of a molecule of the oxide of iron. Let us now return to the first experiment, in which steam is passed over red-hot iron. In this case the motions of the steam molecules are accelerated by the heat to such a degree that some of them are torn asunder, and oxygen and hydrogen atoms are liberated, and mingle with the molecules of steam. If no iron were present, these dissociated atoms of oxygen and hydrogen would occasionally chance to collide with one another again, and in some of these cases the speed of the colliding atoms would not be great enough to prevent them from recombining and forming new molecules of steam. The steam-molecules are therefore always dissociating and re-forming, and it is plain that at any given instant the proportion of such molecules that are in a state of dissociation will be greater, the higher the average speed of the steam-molecules — that is, the higher the *temperature*. As a matter of fact, however, some of the liberated oxygen atoms come in contact

with the iron that is present, and combine with it to form the black oxide; and the hydrogen atoms that were formerly their partners pass on with the steam. In the second experiment the phenomena are very similar. The heat partially dissociates the iron oxide, the oxygen atoms thus liberated find partners among the hydrogen atoms flowing overhead, and the steam thus formed is swept away in the stream of hydrogen, and is prevented from again coming in contact with the reduced iron that has been left behind. Now let us consider the experimental tube to be stopped up at both ends, so that nothing can enter it or leave it. All the various phenomena I have described will then take place simultaneously, and a permanent distribution will presently be reached, in which molecules of iron oxide are dissociating in some places just as fast as molecules of oxygen are combining with metallic iron in other places, and molecules of steam are dissociating just as fast as other molecules of steam are forming. When this condition of equilibrium is established, the composition of the contents of the tube will appear to be constant; but the constancy is only apparent — it is of a statistical nature, just as the constancy of the vapor-density over a liquid is statistical. If the distribution of the various substances in the experimental tube is altered, the balance will be destroyed. For example, if some of the hydrogen is removed, more steam will be dissociated and more iron oxide formed, until the proportion of hydrogen to steam becomes the same as before. Conversely, if some of the steam is removed the iron oxide will be dissociated faster than it is formed, the oxygen thus liberated will combine with some of the hydrogen, and more steam will be formed; and this readjustment will continue until the original proportion of hydrogen to steam is again restored. Hence it is plain that if the steam that is formed is continually swept away by a current of hydrogen, the result will be that the oxide of iron will be all ultimately reduced; while if the hydrogen that is liberated is swept away by a current of steam, the iron will be continuously oxidized, until

it is all converted into oxide. This beautiful explanation of the phenomena is due to Deville, and the principles that underlie his theory have been applied to a wide range of other phenomena, and upon them a complete theory of chemical equilibrium has been erected. I regret that time will not allow me to discuss this most interesting subject further, nor even to give more examples of dissociation; but you will find Guldberg and Waage's generalized theory of chemical equilibrium given in Ostwald's *Outlines of General Chemistry.*

Solutions.* — Many solids, when brought into contact with certain liquids under suitable conditions, cease to exist as solids, and diffuse throughout the liquid in which they are submerged. This process, by which the solid is caused to disappear, is called *solution;* and the same word is also used, as a noun, to signify the liquid that results from the process. In some cases the liquid acts chemically upon the solid, forming a new compound, which remains behind when the solvent is evaporated — an instance of such action being the formation of chloride of sodium when caustic soda is placed in hydrochloric acid. We shall not discuss these cases, but shall confine our attention exclusively to those in which the solvent is not positively known to act chemically upon the dissolved substance — as when sugar is dissolved in water, or silver chloride in dilute ammonia. In such instances we have to think of the molecules of the liquid as exerting a certain attraction on the external molecules of the solid; though we

* In accordance with the general plan of this book, I have included, in the present section, only such points as seem to be well established, and to have an immediate bearing on the molecular structure or deportment of bodies. Our knowledge of solutions is still far from perfect, and the reader will find that chemists are divided, upon this subject, into two great schools or factions. I will not pretend to decide between these factions. The reader may profitably consult the article on *Solutions* in Watts's *Dictionary of Chemistry* (last edition, 1894), where he will find the rival doctrines ably expounded. Ostwald's *Solutions* (London, Longmans, Green & Co., 1891) can also be recommended.

shall be careful not to say much about the ultimate *nature* of this attraction, lest we might give offense to the advocates of one or other of the two schools into which, on this point, chemists are divided. If the attraction of the liquid for the molecules of the solid is slight, the attraction of the molecules of the solid for one another may still greatly preponderate, and in that case there will be no solution, and we shall have merely a solid submerged in a liquid. On the other hand, if the external molecules of the solid are attracted outward by the liquid more powerfully than they are attracted inward by the solid itself, they will be detached, and the solid will rapidly dissolve. In case the attraction towards the liquid is less than that towards the solid, but yet comparable with it, particles will tear themselves loose from the solid and pass into solution, whenever their velocities chance to be great enough to enable them to overcome the excess of attraction towards the solid. In some cases heat will be *evolved* during the process of solution, and in other cases it will *disappear*, or become latent; and we cannot say, in advance, which of these phenomena will take place in any given instance, until we fully understand the nature and magnitude of the various forces that are called into operation. I believe that many of the phenomena of solutions, as well as those of crystallization and other changes of state in bodies, can be explained by means of the single assumption that in every case the molecules of the system tend towards that configuration in which their united potential energy is as small as possible, just as a marble when thrown into a wash-bowl tends continually towards the bottom of the bowl, where its potential energy is least. Thus, when we find that a given solid dissolves in a given liquid, we are to infer that the potential energy of the system is less when the solid is in solution than it is when the solid is intact, and merely submerged in the pure liquid; and when we find that a given solid does *not* dissolve in a given liquid, the converse is to be inferred. I can imagine that you will be ready with the objection that if the potential

energy diminishes, the kinetic energy must increase; and that this would imply that solution is always accompanied by a rise in temperature, which is by no means the fact. You must bear in mind, however, that the properties of solids show that the motions of the molecules of these bodies are restricted in some way, and that the process of solution undoubtedly removes these restrictions, so that when the molecules of the solid mingle with those of the liquid, they acquire a certain additional number of "degrees of freedom." Hence, although the diminution of potential energy certainly does imply an increase in the *total* kinetic energy, it does not by any means imply an increase in the kinetic energy *of translation*. That is, it does not of necessity imply an increase in *temperature*.

Diffusion. — We may apply this same principle of minimum potential energy in discussing the *diffusion* of a dissolved substance through the solvent. Suppose, for example, that we have a solution in which the concentration is different in different regions; then the potential energy of the system, per unit volume, must also be different in different regions; and hence the molecules of the dissolved solid will tend towards the more dilute parts or towards the more concentrated parts, according as the potential energy of the system would be lessened by the one process or by the other. In fact it can be easily shown, by mathematical reasoning, that if the temperature of the solution be maintained constant at all points (so as to avoid thermodynamical considerations), the potential energy of the system will necessarily be least when the concentration is everywhere the same — that is, when the solution is homogeneous. To prove this, let us assume that at the outset the solution proposed for consideration has different degrees of concentration in different parts, and let us conceive it to be divided by imaginary surfaces into a great number of elementary portions, whose volumes are v_1, v_2, v_3, ... Furthermore, let us represent the quantity of dis-

solved substance, per unit volume, in these respective elementary portions, by $c_1, c_2, c_3, \ldots$, and the corresponding potential energies by $p_1, p_2, p_3, \ldots$ Then, representing the total quantity of solid in solution by Q, and the total potential energy of the system by P, we have

$$Q = c_1v_1 + c_2v_2 + c_3v_3 + \ldots \tag{42}$$

and

$$P = p_1v_1 + p_2v_2 + p_3v_3 + \ldots \tag{43}$$

We are required to discover the relations that must exist among the c's, in order that P shall be as small as it can be, consistently with the condition (42). It is shown, in works on the differential calculus, that such problems can be solved by differentiating the expression

$$P - kQ \tag{44}$$

with respect to each of the variables $c_1, c_2, c_3, \ldots$, and equating all the resulting differential coefficients to zero; k being a multiplier at present undetermined, and which, although it may not be a constant, is nevertheless to be treated as such in performing the differentiations. The expression (44) is equivalent to

$$(p_1v_1 + p_2v_2 + p_3v_3 + \ldots) - k(c_1v_1 + c_2v_2 + c_3v_3 + \ldots),$$

and upon differentiating this successively with regard to c_1, $c_2, c_3, \ldots$, and equating the coefficients to zero, we have

$$v_1\frac{dp_1}{dc_1} - kv_1 = 0,\ v_2\frac{dp_2}{dc_2} - kv_2 = 0,\ v_3\frac{dp_3}{dc_3} - kv_3 = 0, \ldots,$$

or, which is the same thing,

$$\frac{dp_1}{dc_1} - k = 0,\ \frac{dp_2}{dc_2} - k = 0,\ \frac{dp_3}{dc_3} - k = 0, \ldots \tag{45}$$

These are the conditions that must subsist in order that the potential energy of the system may have its smallest possible value; and by interpreting them we must discover what relations exist among the c's. Let us assume that

$$p = f(c).$$

Then (45) is equivalent to

$$f'(c_1)=f'(c_2)=f'(c_3)=\ldots=k. \qquad (46)$$

If this relation were a *general* one, we might conclude from it that

$$p=\int kdc;$$

but it must be borne in mind that equations (45) are true *only when the solution under consideration has reached its final condition of equilibrium.* Hence we can infer nothing with regard to the form of the function $f(c)$, and we are driven to the conclusion that (46) is true, when the final state of equilibrium has been attained, regardless of the form of $f(c)$. But that is impossible unless

$$c_1=c_2=c_3=\ldots;$$

that is, unless the concentration of the solution is everywhere the same. There is one point about our analysis that ought to be a little more carefully considered. The differential coefficients of (44) would be equal to zero whether P were a minimum *or a maximum;* and hence our reasoning contains a mathematical ambiguity which must be further examined. If P were a *maximum* when the concentration is everywhere the same, it follows that diffusion would *increase* the differences of concentration that existed in the original solution, until finally the concentration would become zero in some places, and as great, in other places, as the nature of the dissolved substance would allow. In other words, the dissolved substance would be entirely precipitated from solution. The general conclusion to which our mathematical reasoning leads therefore is that if a given solid dissolves in a given liquid, its solution will ultimately become homogeneous; while if it does not dissolve, the reason is that the potential energy of the system is less when the solid is undissolved than it would be if it were dissolved.

Osmotic Pressure. — Passing over the earlier experiments on this subject, I shall proceed at once to those made by Pfeffer. His apparatus is shown in Fig. 40.* It consists essentially of a clay cell, *Z*, whose pores have been closed by a precipitate of ferrocyanide of copper. A cell thus prepared allows water to pass through it freely, but is impervious to such solids as may be dissolved in the water. In using the apparatus the cell, *Z*, is filled with a solution of some substance — say of sugar or nitre — of known strength, and is then immersed in water. It is found, under these circumstances, that water passes from the containing vessel into the clay cell, thereby giving rise to a pressure called the "osmotic pressure," which can be read off by the mercury manometer, *A*, and which is often surprisingly great. To understand this phenomenon we have to fall back once more on our fundamental principle, that when the system is in equilibrium its potential energy is a minimum. As I told you a moment ago, the potential energy of a solution whose temperature is everywhere the same is least when the dissolved substance is uniformly distributed; and it follows that the total potential energy of the liquid system in Pfeffer's apparatus would be lessened if the dissolved solid within the clay cell should diffuse outward into the water in the containing vessel. It cannot diffuse outward, however, for

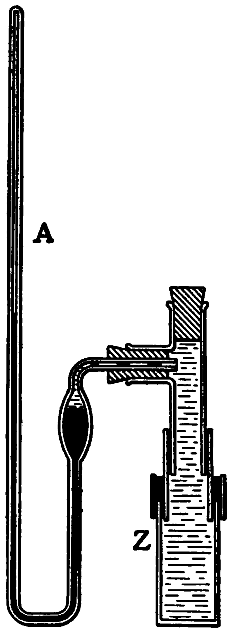


FIG. 40. — PFEFFER'S APPARATUS.

* The cut here presented is taken from that given on page 98 of Ostwald's *Solutions*, to which book the reader is referred for further particulars concerning Pfeffer's experiments, and for detailed information with regard to the preparation of the clay cells.

the cell has purposely been so prepared that it will allow nothing to pass but *pure water*. Hence if the dissolved substance is to become disseminated uniformly throughout the entire mass of water, it will have to do so by some other process. The only other process possible is by the water in the outer vessel *entering the cell;* and, as I have already told you, that is what actually happens. It is another case of Mahomet and the mountain. Water will not pass into the clay cell indefinitely, however, for as soon as the pressure becomes greater inside than it is outside (which happens at the very beginning of the process), energy has to be expended, or stored up, in forcing more water in, against this pressure. The total energy thus expended is equal to the work done in raising the mercury column in the manometer; and water will cease to enter the cell the moment that the energy stored up in the mercury column, owing to the entrance of a small mass of water, becomes equal to the diminution in the potential energy of the system due to the entry of this water. Hence in every case there is a limiting value of the osmotic pressure, depending upon the concentration of the solution and on the nature of the dissolved substance; and this limiting value is usually understood to be meant when the term "osmotic pressure" is used without further qualification. Pfeffer found that a 6 per cent solution of cane sugar gave an osmotic pressure of 307.5 centimeters of mercury, or over four atmospheres. With a 3.3 per cent solution of nitre he obtained a pressure of 436.8 centimeters, or about $5\frac{3}{4}$ atmospheres. Pfeffer also found that the osmotic pressure is proportional to the concentration of the solution, and Van't Hoff has further shown, by thermodynamical reasoning, that it is proportional to the absolute temperature. Hence, if p is the osmotic pressure and v is the number of cubic centimeters of solution that contain one gramme of the dissolved substance, we have

$$p = \frac{R\tau}{v}, \text{ or } pv = R\tau, \tag{47}$$

which is entirely analogous to equation (27), previously established for gases. It will be instructive to examine (47) a little more closely. Suppose, for the moment, that sugar could exist in the form of a gas, without losing its essential properties or undergoing any modification in molecular weight. Then, since the molecular weight of sugar is 342, we know that the density of the sugar-gas would be 171 times the density that hydrogen would have under similar circumstances of temperature and pressure. Now the volume of a gramme of hydrogen, at atmospheric pressure and 0° C., is 11,158 cubic centimeters; and hence the volume of a gramme of sugar-gas, under the same conditions, would be $11{,}158 \div 171 = 65.25$ cubic centimeters. Substituting this for v in the gas-equation (27), and putting $\tau = 273°$ and $p = 1033$ grammes per square centimeter, we find that for *sugar-gas* the constant R would be

$$R = \frac{pv}{\tau} = \frac{1033 \times 65.25}{273} = 247.$$

Returning to equation (47) let us find the value of R that applies when p represents the *osmotic* pressure of sugar. For a one per cent solution, at 0° C., Pfeffer found that $p = 671$ grammes per square centimeter. Hence putting $v = 100$ and $p = 671$, we have, from (47),

$$R = \frac{pv}{\tau} = \frac{671 \times 100}{273} = 246,$$

which is substantially the same as the value we obtained for *sugar-gas*. Ostwald expresses this fact in the following words: "The osmotic pressure of a sugar solution has the same value as the pressure that the sugar would exert, if it were contained *as a gas* in the volume that is occupied by the solution. The gas equation, $pv = R\tau$, holds unchanged, with the same constant, for solutions; only that p here denotes the *osmotic* pressure." This important and suggestive principle was discovered by Van't Hoff. It applies to many substances

besides sugar, and to many other substances it does not apply at all. I cannot digress upon the conditions of its applicability, but must refer you, for further information, to Ostwald's *Outlines of General Chemistry*, and to his *Solutions*. Personally, I am not satisfied that gaseous pressure and osmotic pressure are more than *analogous* with each other, and I strongly question the propriety of saying that "the state of substances in solution is in the widest sense comparable" with the gaseous state.

Electrolysis. — The accepted theory concerning electrolytic action in liquids and solutions was stated by Maxwell with such simplicity that I will read you what he says: "A very interesting part of molecular science, which has not been thoroughly worked out, . . . is the theory of electrolysis. Here an electromotive force acting on a liquid electrolyte causes the molecules of one of its components to be urged in one direction, while those of the other component are urged in the opposite direction. Now these components are joined together in pairs by chemical forces of great power, so that we might expect that no electrolytic effect could take place unless the electromotive force was so strong as to be able to tear these couples asunder. But, according to Clausius, in the dance of molecules which is always going on, some of the linked pairs of molecules acquire such velocities that when they have an encounter with a pair also in violent motion the molecules composing one or both of the pairs are torn asunder, and wander about seeking new partners. If the temperature is so high that the general agitation is so violent that more pairs of molecules are torn asunder than can pair again in an equal time, we have the phenomenon of dissociation, studied by M. St.-Claire Deville. If, on the other hand, the separated molecules can always find partners before they are rejected from the system, the composition of the system remains apparently the same. Now Professor Clausius considers that it is during these temporary separations that the electromotive

force comes into play as a directing power, causing the molecules of one component to move, on the whole, one way, and those of the other, the opposite way. Thus the component molecules are always changing partners, even when no electromotive force is in action, and the only effect of this force is to give direction to those movements which are already going on."*

Saturation. — Thus far we have said nothing about the *quantity* of solid that can be dissolved in a given mass of liquid. In some cases it appears that the solvent is capable of taking up an almost indefinite amount of solid, the resulting "solution" varying from a moist solid to an undoubted liquid; but in most cases the solvent, at any given temperature, can take up only a definite quantity of solid. A solution that contains as much of any given substance as it is capable of dissolving, is said to be *saturated* with respect to that substance. If to such a saturated solution we add more of the solid, we can see no change. The solid that we have added does not lessen, nor does it increase. Such a system is closely analogous to a closed vessel containing a liquid in contact with its saturated vapor; and the explanation of the apparent equilibrium is substantially the same in both cases. The solid *does* lose molecules from its surface, but an equal number return to it from the liquid; and hence the apparent equilibrium and quiescence. If the system is disturbed by altering the temperature, or by evaporating some of the liquid and thus increasing the concentration, the equality of the exchanges that are taking place at the surface of the submerged solid is destroyed, and the concentration of the solution increases or diminishes until a new point of equilibrium is reached, at which the number of molecules leaving the solid in a unit time again becomes equal to the number of those returning to it. By the same kind of reasoning that was employed in considering evaporation from a liquid, we

* Maxwell, *Theory of Heat* (ninth edition, 1888), page 325.

can easily show that the equilibrium between a solid and its saturated solution is entirely independent both of the *quantity* of the undissolved solid, and of the area of its exposed surface.

Distillation. — One of the most striking things about a solution is, that if it is allowed to evaporate, *the solvent passes off alone*, leaving behind it the solid that was previously dissolved. This circumstance, which is of extraordinary value in the arts, seems to be passed over without adequate discussion by writers on the theory of solutions. If the molecules of the dissolved solid are moving freely about among the molecules of the solvent, we should naturally expect them to escape from the surface of the solution with a frequency not altogether insensible in comparison with the frequency of escape of the solvent-molecules; but this is not the fact. If, as the advocates of the "hydrate theory" of solutions believe, the dissolved substance is combined with the solvent in some manner, so that its molecules are relatively massive, — and if, furthermore, there is, for liquids, some proposition analogous to Boltzmann's law of distribution of kinetic energy in gases, — then it might follow that no sensible proportion of the ponderous, hydrated molecules of the dissolved substance can ever move fast enough to overcome the attraction of the liquid, and escape from it by the process of evaporation. On the other hand, if any considerable proportion of the molecules of a dissolved electrolyte are simultaneously in a state of dissociation (as maintained by the advocates of the "physical theory" of solutions), it is not easy to see how an adequate, mechanical explanation of the facts of distillation can be given. I make this statement solely as a confession of my own ignorance, and the advocates of the "hydrate theory" of solutions are welcome to such comfort as they can extract from it. Of course we can always fall back on the fact that most solids are non-volatile at temperatures to which their solutions are ordinarily submitted. This, together with the further fact that solution implies a fall in potential energy,

might be considered as affording a basis for explaining the fixity of dissolved substances; for if the external molecules of the solid were originally held in place by the attraction of the solid, and if the attraction of the liquid for these molecules is greater than the attraction of the solid for them, then one might possibly infer that the non-volatility of the original solid implies its non-vaporization from solution. But I strongly doubt if this argument would commend itself to one who did not know the facts in advance. Moreover, it is not a mechanical explanation at all, in the sense in which I understand the phrase.

Supersaturation. — If we cool a saturated solution of a substance that is more soluble at higher temperatures than at lower ones, under ordinary circumstances there will be a deposition of the solid. If, however, care is taken to exclude all traces of *free* solid from the solution, the cooling may often be carried to a point considerably below the temperature normally corresponding to the given degree of saturation, without deposition taking place. Solutions in this condition are said to be *supersaturated.* If I have made myself intelligible in explaining the phenomena of *saturation,* you will have no difficulty, I think, in understanding *supersaturation.* The concentration of a solution containing an excess of solid is determined by the equality of the molecular exchanges that take place at the surface of the solid; and hence it is plain that when no such free solid is present, the cause that normally determines the degree of concentration is also not present, — and, in fact, the conception of a definite point of "saturation" is no longer applicable. If a particle of the dissolved solid, or of a substance isomorphous with it, be placed in a supersaturated solution, the dissolved substance is rapidly deposited about the submerged particle as a nucleus, until the concentration of the solution is reduced to its normal value. A solution cannot be cooled indefinitely, without deposition, even when all free solid is excluded with the

greatest care. The reason for this seems to be, that in the ceaseless re-arrangement of molecules that takes place in a liquid, it occasionally happens that a certain number of molecules of the dissolved substance fortuitously come together in such a way as to serve as a nucleus for the deposition of the solid; and when this occurs, the supersaturated solution spontaneously deposits the excess of solid that it contains.

Crystals. — The fundamental fact of crystallization is thus lucidly stated by Williams*: "All chemically homogeneous substances, when they solidify from a state of vapor, fusion, or solution, tend to assume certain regular polyhedral forms. This tendency is much stronger in some substances than in others, and it varies widely in the same substance under different physical conditions. The regularly bounded forms thus assumed by solidifying substances are called *crystals*." Crystals of different substances have different shapes, and sometimes the same substance is deposited in different forms under different conditions. But it is not alone in the regularity of their shape that crystals are peculiar. If we examine these bodies we find that, in general, they exhibit different properties in different directions. Homogeneous, uncrystallized bodies, such as glass, exhibit the same cohesion, the same hardness, the same elasticity, and the same thermal, optical, and electrical properties, wherever we examine them; but in crystals it is found that, with certain exceptions, these properties are the same along directions that are *parallel*, but different along directions that are not parallel. In other words, homogeneous, uncrystallized bodies are *isotropic;* while crystals, generally speaking, are not isotropic. These points are described in all the works on crystallography, but crystals also exhibit many other interesting properties which are seldom discussed in such books or journals as are accessible to the general public. For example, if a crystal be removed from a solution in which it is forming, and be carefully pre-

* *Elements of Crystallography*, page 1.

served, it never loses the power of resuming its growth. If at any future time it is submerged in a solution similar to that in which it was first formed, the invisible forces again assert themselves, and the crystal slowly enlarges, precisely as if there had been no interruption. A crystal may even have been produced in some former geological period, thousands of centuries ago; and yet, upon placing it in a suitable solution, we find that the work of molecular architecture is at once resumed, just as though all those intermediate ages were blotted out. The crystal may even be almost entirely destroyed in the interval of inactivity, and yet it will grow as before, provided there remains within it some small fragment that has the structure of the primitive crystal. Crystals also possess the power of self-repair to a considerable extent, so that if they are scored or bruised the subsequent growth is abnormally rapid over the injured areas, until the injuries disappear and the crystal regains its perfect form.*

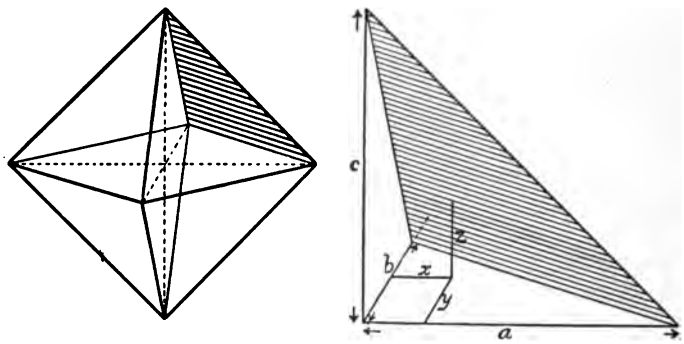
Bounding Planes of Crystals. — In order to facilitate the discussion of the planes that form the limiting surfaces of a crystal, let us conceive axes to be drawn within the crystal, and let us refer the bounding planes to these axes, precisely as we do in the study of analytical geometry of three dimensions. The positions of the axes are to be determined by considering the *symmetry* of the crystal; but as you have no doubt made some study of crystals in connection with your courses in geology and mineralogy, I shall not dwell upon the assignment of axes in the various systems of crystals that occur in nature, but shall assume that they are already drawn. Let us therefore pass to the consideration of some actual crystal — for example, the typical octahedral form shown in Fig. 41. This crystal is *perfect* — that is, it is symmetrical with respect to each of the three axes (shown by the dotted lines), and it is not modified by the loss of its edges, nor in

* See Professor John W. Judd's excellent discourse, *The Rejuvenescence of Crystals*, in *Nature* for May 28, 1891.

any other way. Fig. 42 is an enlarged view of the shaded face of Fig. 41, and with the notation given in the figure it is plain that the equation of this face is

$$\frac{x}{a}+\frac{y}{b}+\frac{z}{c}=1. \tag{48}$$

It is also evident that all the other faces of this crystal are obtainable from (48) by changing the sign of one or more of the quantities a, b, and c. A similar equation can be found for each face of any given crystal whatever; and observation



FIGS. 41 and 42. — ILLUSTRATING THE GEOMETRY OF A CRYSTAL.

indicates the very remarkable fact that in all planes that actually *occur* in crystals, the quantities a, b, c, either bear a *simple ratio* to one another, or are infinite. For example, if the equation of any given crystal-face were found, we might have

$a:b:c=1:2:2$, or $a:b:c=4:5:6$, or $a:b:c=2:3:\infty$,

or some other similar proportion; but we should never find any crystal plane in which the ratio was anything like this:

$$a:b:c=1:7:\sqrt{13}.$$

This law — called the "law of rationality of the intercepts" (or indices) — like many another one in the domain of physics, is seldom fulfilled with *strict accuracy;* and yet it

comes so near the truth that we must regard it as the visible expression of some structural simplicity within the crystal.*

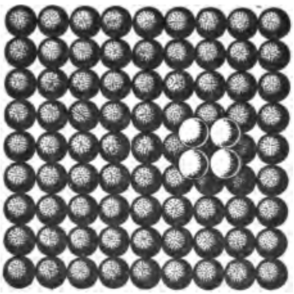
Molecular Structure of Crystals. — The molecular structure of crystals has been investigated by Sohncke and others from a geometrical standpoint,† but I prefer to give you what may be called a "physical" presentation of the subject, following Professor Liveing for the most part.‡ Very little is known about the constitution of solid bodies generally, but it is quite certain that in *crystals* there is some regularity of *orientation*, either in the molecules themselves or in their motions. The physical properties of these bodies seem to prove that much, beyond a reasonable doubt. We shall take it for granted that this regularity is of such a nature that any given molecule, in its vibratory excursions, never passes outside of a certain imaginary ellipsoid which we may conceive to be described about the mean position of the molecule. Crystals may then be regarded as aggregates of such ellipsoids, piled up in such a way that the corresponding axes of all of them are either parallel throughout the mass, or at least arranged in accordance with some definite geometrical scheme. If we now apply our general principle, that the potential energy of a molecular system tends towards a minimum, we see that when a substance solidifies, either from solution or from a state of fusion, the ellipsoids that bound its molecules must take such positions that the potential energy of the resulting solid is as small as possible. I shall assume that the constitution and mode of motion of the molecules under consideration are such that the potential energy of the system is least when the

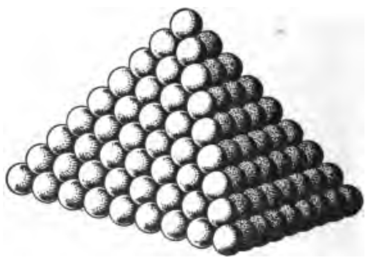
* For a more accurate form of the law of rationality of the indices, see the article on *Crystallization* in Watts's *Dictionary of Chemistry*. See also Williams's *Crystallography*.

† See the chapter on *Crystals* in Ostwald's *Outlines of General Chemistry*, where the geometrical theory is very clearly set forth.

‡ *Nature*, June 18, 1891, page 156. I am hardly prepared to follow Professor Liveing in extending the conception of "surface tension" to solids, however.

ellipsoids are piled together as closely as possible; though, as I have already told you, this is by no means a necessary assumption, nor is it, speaking generally, even a probable one. Moreover, as we are touching upon this subject for the sole purpose of showing *how* the molecular theory explains crystal forms, and without any intention of discussing the constitution of these bodies exhaustively, I shall not treat of the general case in which the axes of the ellipsoids are unequal, but shall confine myself to that special one in which they are equal, and the ellipsoids are spheres. As Professor Liveing remarks, "the problem is then reduced to finding how to pack the greatest number of equal spherical balls into a given space." You will find it interesting and instructive to work out this problem, during some leisure hour, with the help of a liberal supply of buck-shot or bullets. Three possible solutions of it will readily occur to you. In the first place, we can arrange a layer of spheres as shown in Fig. 43, where each sphere touches four others; and upon this layer we can place another one in the manner illustrated by the four

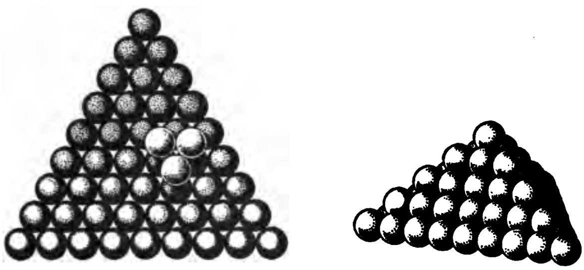




FIGS. 43 and 44.—SQUARE PYRAMID OF SPHERES.

lighter spheres in the figure — each sphere in the second layer coming directly over one of the interstices in the first one. By adding other layers in the same way, we shall eventually form the pyramid shown in Fig. 44. A second method of

arranging the spheres of the first layer is shown in Fig. 45, where each of the interior spheres touches *six* others. If a second layer be superposed upon this first one *in the manner indicated by the three light spheres*, and the piling is continued in the same manner, we shall eventually arrive at the form of



FIGS. 45 and 46. — TRIANGULAR PYRAMID OF SPHERES.

pyramid shown in Fig. 46. You will find that there are *two ways* of placing the second layer upon the fundamental one shown in Fig. 45. One of these methods, if continued, gives the pyramid shown in Fig. 46, while the other gives a pyramid of greater height. Fig. 46 is really half of a cube, its apex being a corner of the cube. The other pyramid to which I have referred is a regular tetrahedron, formed on Fig. 45 as a base. Now although these three methods of arranging the spheres may seem to you, at first sight, to be distinct, a little thought (assisted perhaps by your experimental pile of bullets) will show you that the internal structure is identical in all of them. The spheres in any one of the slant faces of Fig. 44 are arranged precisely like those in Fig. 45; and the slant faces of Fig. 46, on the other hand, correspond exactly to the configuration shown in Fig. 43. There is only one "closest way" to pack the spheres, and if they are piled in that way, all the pyramids that I have referred to can be obtained by passing suitable planes through the mass. I must now refer briefly to what may perhaps be called the fundamental fact of crystallization — the fact, namely, that

the bounding surfaces of crystals are *planes*. When a crystal is forming, we have to conceive that a continuous series of exchanges is going on, all over its surface. Molecules of the dissolved substance are caught by the attraction of the growing crystal, but, on the other hand, molecules of the crystal are continually passing into solution again; and the gradual increase in size of the crystal is due to the fact that in a unit time more molecules are caught by it than are lost again. With this much premised, let us turn our attention to Fig. 47, which represents a sphere-pyramid (or crystal) similar to that in Fig. 44, except that it has a partially completed layer on one face. Let us see what will happen as the deposition of spheres proceeds. If a sphere should lodge against a slant face of Fig. 47, it would touch *three* spheres of the pyramid, and the force of attraction exerted upon it by the molecules within these spheres would be the chief cause of its retention as part of the crystal. Let us next assume that a sphere lodges on the little ledge formed by the top of the partial layer shown on the right. It will then touch *five* spheres, and will be held in position by the attractions of the five corresponding molecules. You will readily see, I think, that as the molecules of the crystal are torn off, in the process of re-solution that is ever going on, those that have adhered to the slant face of the crystal will be torn away with greater frequency than those that have lodged on the little ledge. It follows that whenever a few molecules happen to be deposited in juxtaposition on the face of a crystal, the growth about the edges of the layer thus begun will be far more rapid than the sporadic growth that occurs elsewhere, and the layer will be quickly extended until it covers the entire face of the crystal.

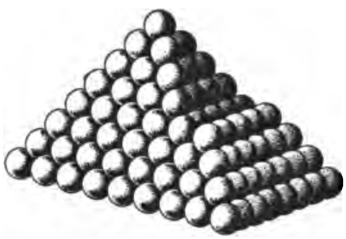


FIG. 47. — SQUARE PYRAMID WITH PARTIAL LAYER OF SPHERES ON ONE SIDE.

Hence if the faces of the crystal are plane at any one moment of its growth, they will always remain so; and as the imaginary surfaces that enclose the group of four or more spheres that constitute the beginnings of a crystal can be regarded as planes, the reason for the flatness of the faces of the finished crystal becomes apparent. If you will consider the bottom face of Fig. 44 in this same manner, you will find that it will grow considerably faster than the slant faces, and that the crystal will tend towards the octahedral form that would be obtained by placing two of these square pyramids base to base. The self-repair of crystals is also explicable by the same line of reasoning. We do not yet fully understand the phenomena of crystallization, and hence we are by no means completely prepared to explain them. The same substance will often crystallize in different forms under different conditions, and I suppose we must conclude from this that the tendency of the molecule-spheres to adhere to the various faces of the growing crystal is not altogether independent of the circumstances under which the deposition takes place. You will find, by once more referring to your bullets, that the planes that I have shown in the diagrams are by no means the only ones that can be used to cut out crystalline forms from the closely-piled spheres. The planes that I have shown are those that have the simplest relations among their "indices," or intercepts; and you will find, by trying other planes, that the faces of the pile become increasingly irregular as the ratios of the intercepts of these planes depart further from those ratios that can be expressed by small integers or simple fractions. This gives us a suggestion of the meaning of the "law of rationality of the intercepts," but I cannot develop this suggestion further at the present time. There is one other point that I must touch upon, before leaving this fascinating subject of crystal forms, and that is, the existence of planes of easiest *cleavage.* If we try to split a crystal, the crack, once started, will naturally tend to follow the direction of least resistance; and this direction will be that in which the number of sphere-

contacts, per unit area of fractured surface, will be least. There is no difficulty in investigating this number of contacts along any given plane — that is, there is no difficulty except that the labor is sometimes quite considerable. It is easy to show, for example, that in the cubical crystal of which Fig. 46 is one half, the number of sphere-contacts that must be broken, per unit area of fractured surface, is

$$\frac{2\sqrt{3}}{d^2} \tag{49}$$

when the fracture is parallel to the base of Fig. 46, and

$$\frac{4}{d^2} \tag{50}$$

when it is parallel to the front face of this figure (d being the diameter of a sphere). Now (49) is less than (50), and hence the crystal can be broken along a direction parallel to the base of Fig. 46 easier than it can be along a direction parallel to one of the cubic faces of the crystal. This corresponds to the known fact that in cubical crystals the cleavage is usually octahedral. I have tried to give you the barest outline of the application of the molecular theory to crystalline bodies, and I should like to dwell longer upon it, were it not for the fact that the subject is so extensive that no adequate presentation of it could be given in any reasonable time. There is abundant room for research here, too; for the crystal-theory has by no means attained its final form. We have, as yet, only some very general notions concerning it; and if I have succeeded in showing you the *direction* in which future research is likely to lead us, I have accomplished all that I could hope to, in the short time at my disposal.

V. MOLECULAR MAGNITUDES.

Preliminary Remarks. — Before entering upon a discussion of the sizes of molecules, or of the range of molecular forces, we ought to have a clear idea of what is meant by these terms. Unfortunately we do not yet know enough about molecules even to define, in a satisfactory manner, what is meant by their "size." If they were hard, smooth, material spheres, we should know what is meant by the word; but if they have any other shape, or any other constitution, its meaning is not so clear. Even if molecules were hard bodies of definite form, we ought to specify *which one* of their dimensions is intended when we speak of their "size"; but in the present state of knowledge this is utterly impossible, and hence it is also impossible to compute the dimensions of molecules with any considerable approach to precision. We have had to be contented, thus far, with determinations of the general *order of magnitude* which must be assigned to these bodies; and it is in this sense alone that I shall speak of the "size of molecules" this evening. In the original form of the kinetic theory of gases the molecules were assumed to be spherical, in spite of the fact that they were believed to have other forms, because such a supposition simplified the mathematical treatment of the subject; and in our attempts to discover the sizes of the molecules we shall again assume them to be spherical, for the same reason, and with the same justification. We shall treat them as spheres, having a diameter which represents, in some sense, the average diameter of the actual molecules. With this much premised, let us proceed to review a few of the methods that have been proposed for finding molecular magnitudes.

The Electrical Method for Finding the Aggregate Volume of Molecules. — It has been suggested that the aggregate volume of the molecules of mercury vapor can be found by

the following electrical method:* There is some reason for believing that the molecules of mercury vapor actually are spherical [see page 52]; and if we further assume that they are capable of conducting electricity, it can be shown that the "specific inductive capacity," K, of the vapor, can be calculated by means of the formula

$$K=\frac{1+2\epsilon}{1-\epsilon}, \tag{51}$$

where ϵ stands for the ratio which the aggregate volume of the spherical molecules bears to the total space in which they are confined. By solving this equation for ϵ we have

$$\epsilon=\frac{K-1}{K+2},$$

from which we could compute ϵ if we knew K. I do not find that the specific inductive capacity of mercury vapor has ever been determined, and hence I cannot show you the numerical result that the electrical method would give. Since equation (51) can be deduced only when the molecules are known to be conducting spheres, it is manifestly unfair to apply it to such gases as hydrogen and oxygen, whose molecules are certainly not spherical. If we knew the *forms* of the molecules of these gases it might be possible to construct some equation analogous to (51), which would be applicable to them; but in the absence of such knowledge it does not appear profitable to dwell longer upon the electrical method for determining the aggregate volume of molecules.

Aggregate Volume of Molecules, from the Gas Equation.— If we return to the corrected gas equation, as given by Clausius for carbon dioxide (30), and consider the effect of putting $v=b$ in that equation, we shall see that the result would be to make $p=\infty$. Now we cannot imagine that the molecules of a gas, when under an infinite pressure, could still remain at any finite distance from one another; and

* See *Encyclopædia Britannica*, article *Molecule*, page 620.

hence we infer that if the volume of a given mass of carbon dioxide should be reduced, by pressure, until $v = b$, the molecules of this mass of gas would be brought into absolute contact with one another. The value of b, as given by Clausius, is .000843; and we infer from this that the total space required for the molecules of carbon dioxide, when these molecules are in contact with one another, is .000843 of the space occupied by the gas at the freezing point of water, and under atmospheric pressure. However, this space is not all actually occupied by the molecules, for there must be vacant interstices. In fact, it is easily shown that if the molecules are spheres, packed together in the closest way possible, the *actual* aggregate volume of the molecules will be very nearly $\frac{6}{7}$ of their apparent volume; and hence we conclude that in carbon dioxide the actual aggregate volume of the molecules is $\frac{6}{7} \times .000843 = .000723$ of the space occupied by the gas itself at 0° C. and atmospheric pressure. "Corrected" equations have been given for other gases by various observers, and from these, by a process of reasoning precisely like that I have just given you, the aggregate molecular volumes of the corresponding gases may be obtained. Thus from equations given by Mr. William Sutherland* I have obtained the following values of the aggregate molecular volumes of certain gases, the unit in each case being the volume of the gas itself at 0° C. and one atmosphere pressure. For H, $\epsilon = .00033$; for N, $\epsilon = .00087$; and for O, $\epsilon = .00074$.

Remarks on the Foregoing Results. — If the volume of the molecule is unaltered when a substance passes from the gaseous to the liquid and solid states, it is evident that we have a sort of check which can be applied to the results we have just obtained, so far as the available experimental data will allow. Thus, if we should compress carbon dioxide until its molecules were brought into absolute contact with one

* See his paper on *The Laws of Molecular Force*, in the *Philosophical Magazine* for March, 1893, page 232.

another, the volume of the resulting mass would be .000843 of the volume occupied by the gas at 0° C. and under atmospheric pressure. The *density* of this mass would therefore be equal to the density of the original gas divided by .000843. Now Regnault found that at 0° C., and one atmosphere pressure, a cubic decimeter of carbon dioxide weighs 1.9774 grammes; and therefore the weight of a cubic decimeter of carbon dioxide molecules, when in actual contact, is $1.9774 \div .000843 = 2.346$ kilograms. This is the greatest density carbon dioxide could have, in any form, if our calculations are correct, and if the molecules of this gas preserve their bulk when the gas changes its state. The greatest observed density that I know of, for this gas, is 1.6 kilograms per cubic decimeter. This value was observed in carbon dioxide that had been solidified and hammered. The greatest observed density, you will see, is only about two-thirds of the maximum possible limit as given by our computation. Similar calculations are readily made for the remaining three gases for which we have computed the value of ϵ. The results are as follows:

MAXIMUM DENSITIES OF H, N, O, AND CO_2.

GAS.	NORMAL DENSITY.*	GREATEST POSSIBLE DENSITY (Calculated).	GREATEST OBSERVED DENSITY.
Hydrogen	0.0896 gms.	0.232 kg.	0.089 kg.
Nitrogen	1.2562	1.232	0.905
Oxygen	1.4298	1.653	1.24
Carbon dioxide . .	1.9774	2.346	1.60

The "greatest observed densities" here quoted are from the following authorities: For hydrogen I have taken the density at 3,000 atmospheres, as given by Amagat's experiments, and quoted in Preston's *Theory of Heat;* for nitrogen I have

* That is, the "weight of a cubic decimeter, in grammes, at 0° C. and one atmosphere pressure." The densities in the last two columns of the table are expressed in *kilograms* per cubic decimeter.

taken Olszewski's greatest result, obtained at $-194°$ C.; for oxygen I have taken Wroblevsky's result, obtained at $-200°$ C.; and the density given for carbon dioxide is due to Dewar. By observing the increase in volume of palladium when this metal is caused to occlude a given weight of hydrogen, Dewar inferred that the density of the occluded hydrogen may be as great as 0.623; but no direct measure of the density has ever given anything approaching this figure, which is seven times the maximum observed value quoted in the table. It seems fair to conclude, therefore, that we are to explain this great apparent density in some other way. It is not unlikely, for example, that the occluded hydrogen is combined with the palladium so as to form a hydride, Pd_2H. Dewar himself suggests this, but he computes the density of the hydrogen as though there were no such combination. So far as I am aware, there is no sufficient reason for supposing that the volume of a molecule remains unchanged when this molecule combines chemically with another one; and hence the high density obtained by Dewar does not necessarily refute the computations we have made. Another point to which I should like to call your attention is, that the numbers we have obtained show that in gases under ordinary conditions the average distance from any given molecule to its nearest neighbor is only about 10 or 15 times the diameter of a molecule. For example, let us conceive the molecules of a mass of carbon dioxide to be suddenly arrested in their motions, and to be rearranged so as to be spaced at uniform distances from one another. Then let this idealized gas be reduced in volume by causing the molecules that compose it to approach one another uniformly until they touch. The distance from the center of one molecule to the center of the next one is then equal to the diameter of a molecule; and the volume of the resulting mass is .000843 of the volume of the original gas. Then since the linear dimensions of similar bodies are to one another as the cube roots of the corresponding volumes, we have the proportion

ORIGINAL CENTRE DISTANCE : DIAMETER OF A MOLECULE

$$= \sqrt[3]{1} : \sqrt[3]{.000843}$$

from which it follows that in carbon dioxide at 0° C. and under atmospheric pressure, the average distance from the center of any one molecule to the center of its nearest neighbor is about $10\frac{1}{2}$ times the diameter of a molecule. Similar computations for the other gases show that the corresponding molecular distance is about 14 diameters in hydrogen, 10 diameters in nitrogen, and $10\frac{1}{2}$ diameters in oxygen. (These results justify the remark on page 14, where the popular comparison of molecular dimensions with stellar dimensions is pronounced erroneous.)

Molecular Diameters by Clausius's Equation. — As long ago as 1858 Clausius published the following remarkable theorem concerning the diameters of gas-molecules: If the average free path be multiplied by 8, the product will bear the same ratio to the diameter of the molecule that the total space containing the gas bears to the space actually occupied by the molecules. At the time this theorem was published, Maxwell's law of the distribution of velocities in gases had not been discovered, and Clausius, in his investigations, had assumed the molecules to have substantially the same velocities throughout the gas. Maxwell's subsequent researches made it possible to take account of the differences in velocity that exist among the molecules of a given mass of gas, and when this had been done it was found that the same theorem holds true, except that in the place of the numerical factor 8 we must use $6\sqrt{2}$ $(=8.485)$; so that in its corrected form Clausius's theorem is as follows:*

$$\frac{8.485\,\lambda}{\delta} = \frac{V}{v} = \frac{1}{\epsilon}, \tag{52}$$

* This equation is readily obtained from Clausius's *Kinetische Theorie der Gase* (1889–91), page 65, equation (20), by multiplying both sides of his equation by $\frac{6\sqrt{2}}{\sigma}$, and observing that $\frac{1}{6}\pi\sigma^3 N$ is the actual volume of the molecules that exist in the volume V of the gas.

where λ is the average free path, δ is the mean diameter of the molecule, and ϵ is the actual united volume of the molecules that exist in a unit volume of the gas. All of these quantities, except δ, can be determined by methods that I have given you this evening; and hence equation (52) enables us to calculate δ, the diameter of the molecule. If we preserve only one decimal place in the numerical factor we shall have 8.5 instead of 8.485, and as this is quite a sufficient approximation for our present purpose, we may write (52) thus:

$$\delta = 8.5\,\lambda\epsilon. \tag{53}$$

In the accompanying table I have collected the values we have obtained for λ and ϵ, and the values of δ that are obtained by substituting these quantities in (53).

MOLECULAR DIAMETERS BY CLAUSIUS'S METHOD.

GAS.	λ	ϵ	δ	
Hydrogen . .	.000 01690 cm.	.00033	47×10^{-9} cm.	19×10^{-9} in.
Nitrogen . .	.000 00903	.00087	67×10^{-9}	27×10^{-9}
Oxygen . . .	.000 00964	.00074	61×10^{-9}	24×10^{-9}
Carbon dioxide	.000 00631	.00072	39×10^{-9}	15×10^{-9}

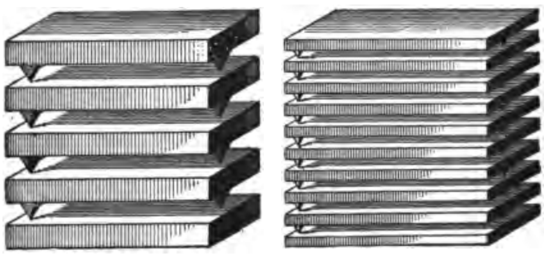
If you are not familiar with the notation used in the last two columns I will explain that 15×10^{-9}, for example, signifies that 15 is to be divided by the ninth power of 10. Hence the molecule of carbon dioxide has a diameter of .000,000,015 of an inch, and if 67 millions of them were placed in contact with one another in a straight line, the row thus formed would be one inch long.

Lord Kelvin's Electrical Method. — Clausius's method, which I have just explained to you, purports to give us the actual mean diameter of a molecule, while most of the other methods give us merely minimum or maximum limits to their sizes, between which limits their true size must lie. Lord

Kelvin's electrical-potential method is one of the most important of those that have been proposed to fix the smallest admissible size of molecules, and I will explain it to you as briefly as I can, following his own words as closely as may be.* He considers the attraction that exists between plates of copper and zinc, when they are put in metallic connection with each other. It is well known that under such circumstances the two metals assume different electrical potentials, and by observing their difference of potential we can compute the attractive force that they exert upon each other, even when this force is so small that it cannot be weighed or otherwise determined directly. "If I take these two pieces of zinc and copper and touch them together at the two corners," he says, "they become electrified, and attract each other with a perfectly definite force, of which the magnitude is ascertained from absolute measurements in connection with the well-established doctrine of contact electricity. I do not feel it, because the force is very small, but you may do the thing in a measured way; you may place a little metallic knob or projection of $\frac{1}{100000}$th of a centimeter on one of them, and lean the other against it. Let there be three such little metal feet put on the copper; now touch the zinc plate with one of them, and turn it gradually down till it comes to touch the other two. In this position, with an air-space of $\frac{1}{100000}$th of a centimeter between them, there will be positive and negative electricity on the zinc and copper surfaces respectively, of such quantities as to cause a mutual attraction amounting to 2 grammes weight per square centimeter. The amount of work done by the electric attraction upon the plates while they are being allowed to approach one another with metallic connection between them at the corner first touched, till they come to the distance of $\frac{1}{100000}$th of a centimeter, is $\frac{2}{100000}$ths of a centimeter-gramme, supposing the area of each plate to be one square centimeter ... Now let a second plate of zinc be brought by a similar process to the other side of the plate

* See his *Popular Lectures and Addresses*, Vol. I, page 168.

of copper; a second plate of copper to the remote side of this second plate of zinc, and so on till a pile is formed consisting of 50,001 plates of zinc and 50,000 plates of copper, separated by 100,000 spaces, each plate and each space being $\frac{1}{100000}$th of a centimeter thick. The whole work done by electric attraction in the formation of this pile is two centimeter-grammes. The whole mass of metal is eight grammes. Hence the amount of work is a quarter of a centimeter-gramme per gramme of metal." By taking account of the mechanical equivalent of heat, and of the specific heats of zinc and copper, it appears that the amount of work thus done by the



FIGS. 48 and 49.—ILLUSTRATING LORD KELVIN'S ELECTRICAL METHOD.

electric attraction would suffice to warm the pile by only $\frac{1}{18130}$th of a Centigrade degree. "But now let the thickness of each piece of metal and of each intervening space be $\frac{1}{100000000}$th of a centimeter, instead of $\frac{1}{100000}$th. The work would be increased a millionfold unless $\frac{1}{100000000}$th of a centimeter approaches the smallness of a molecule. The heat equivalent would therefore be enough to raise the temperature of the material by 62° C. This is barely, if at all, admissible, according to our present knowledge, or, rather, want of knowledge, regarding the heat of combination of zinc and copper. But suppose the metal plates and intervening spaces to be made yet four times thinner, that is to say, the thickness of each to be $\frac{1}{400000000}$th of a centimeter. The work and its heat equivalent will be increased sixteenfold. It would

therefore be 990 times as much as that required to warm the mass by one degree Centigrade, which is very much more than can possibly be produced by zinc and copper in entering into molecular combination. Were there in reality anything like so much heat of combination as this, a mixture of zinc and copper powders would if melted in any one spot, run together, generating more than enough heat to melt them both throughout; just as a large quantity of gunpowder if ignited in any one spot burns throughout without fresh application of heat." This argument shows that it would not be possible to make plates of such an exceeding thinness without splitting molecules. If, as Lord Kelvin suggests, a temperature elevation of 62° C. "is barely, if at all, admissible," it follows that $\frac{1}{100000000}$th of a centimeter is the minimum admissible size of the molecules of copper and zinc; or else (which may in reality be substantially the same thing) that when these metals combine in an alloy, their molecules do not approach one another nearer than this. Expressed in the notation of the table I gave you a few moments ago, this limit is 10×10^{-9} cm., or 4×10^{-9} in. It is interesting to observe the substantial agreement between the results of such radically different methods as Clausius's and Lord Kelvin's, especially as there is no *à priori* reason, so far as I know, for supposing that the molecules of zinc and copper are anything like those of hydrogen, oxygen, nitrogen, and carbon dioxide, in size or in any other respect.

Method by Camphor Movements. — In speaking of the molecular theory of liquids I told you something about the motion of particles of camphor on the surface of water, and I called your attention to the fact that to ensure success in the experiment it is necessary to have the water-surface perfectly clean. The least trace of oily matter checks the camphor-movements quite sensibly; and this fact has suggested a simple method of determining a maximum limit to the size of molecules. Instead of explaining this method in the abstract,

I will tell you how Lord Rayleigh put it into practice.* He provided a circular "sponge bath," 84 centimeters in diameter, and having cleaned it carefully he allowed pure water to flow into it to a depth of several inches. Camphor scrapings were deposited on the water at several places widely removed from one another, and these at once exhibited vigorous movements. A fine platinum wire was then weighed, touched with olive oil, and re-weighed; after which it was cautiously applied to the water-surface. The oil spread over the water, and the experimenter noted the effect on the camphor particles. In one case in which he notes that there was "just about enough" oil to stop the movements, the weighings of the platinum wire indicated that 0.81 of a milligram of oil had been added — that is, 0.00081 of a gramme. Now a cubic centimeter of olive oil weighs about 0.9 of a gramme; and hence it follows that the volume of oil applied was $0.00081 \div 0.9 = 0.0009$ cc. The area of the sponge bath being $.7854 \times 84^2$ square centimeters, the volume of the film of oil that sufficed to still the movements was $.7854 \times 84^2 \times t$, where t is the unknown thickness of the film. Assuming that the volume of olive oil remains constant under the given conditions, we have

$$.7854 \times 84^2 \times t = 0.0009 \text{ cc.},$$

whence $t = 163 \times 10^{-9}$ centimeters, or 65×10^{-9} inches. Now we do not know that this film of oil is just one molecule thick, but we do know that it is *not thinner* than that. Hence Lord Rayleigh's method gives us a *maximum limit* to the size of a molecule of olive oil.

The Surface Tension Method. — This method is due, I believe, to Lord Kelvin; but I am going to give you a presentation of it that is slightly different from his. Let us consider a mass of liquid whose surface tension is S grammes

* Lord Rayleigh's paper, read before the Royal Society in March, 1890, is reproduced in Lord Kelvin's *Popular Lectures and Addresses.*

per linear centimeter. Now if the surface of this liquid be extended in any manner until it increases by the small amount ΔA, the work done against the surface tension will be $S \,.\, \Delta A$. Lord Kelvin has shown, however, that a liquid is *cooled* by extending its surface, and hence the entire quantity of energy required to increase the surface is not fairly represented by $S \,.\, \Delta A$, for we are assisted by the sensible heat that disappears during the process of extension. The results of this thermal effect have been investigated by thermodynamical methods,* and it has been proved that if we keep the temperature constant by adding heat from without, and thus maintain the heat-energy of the liquid constant, the entire expenditure of energy required to increase the surface by an amount ΔA can be written in the form $mS \,.\, \Delta A$, where m is a certain numerical factor dependent upon the nature of the liquid, and upon the constant temperature at which the experiment is performed. For water at ordinary temperatures $m = 1.5$, approximately. What we have really done, in extending the surface of the liquid, is to bring more particles of it out from the interior: we have, in fact, brought to the surface a sufficient number of molecules to form a layer whose area is ΔA, and whose thickness is the diameter of a molecule (which we will represent by δ). The volume of this layer is $\delta \,.\, \Delta A$, and its weight is $w \,.\, \delta \,.\, \Delta A$, where w is the weight of a unit volume of the liquid. Now we have already found the work required to bring a unit weight of liquid to the surface, and I have given you a table of values of it, for four different liquids [page 101]. The work that would have to be expended in order to bring to the surface the layer we are considering is found by multiplying $w \,.\, \delta \,.\, \Delta A$ by the value of $\frac{W}{2}$ for the corresponding liquid; and since it must also be equal to $mS \,.\, \Delta A$, we have the equation

$$\frac{W}{2} \,.\, w\delta \,.\, \Delta A = mS \,.\, \Delta A,$$

* The investigation is given in the Appendix.

or, dividing by ΔA and solving for δ,

$$\delta = \frac{2\,mS}{wW}. \tag{54}$$

From this equation I have prepared the accompanying table, which gives the values of δ for those liquids for which we have previously computed W. The chief weakness of the surface-tension method consists in the underlying assumption that the surface of a liquid is a perfectly definite thing — which, as I have endeavored to illustrate in Fig. 27, is far

MOLECULAR DIAMETERS BY THE SURFACE TENSION METHOD.

LIQUID.	S	m*	w	W	δ
				(cm.-gms.)	(cm.)
Water	.074	1.57	1.00	18.6×10^{6}	12×10^{-9}
Alcohol.	.026	2.36	0.82	3.5×10^{6}	43×10^{-9}
Bisulphide of Carbon . .	.033	2.16	1.29	1.8×10^{6}	61×10^{-9}
Mercury	.551	1.17	13.60	2.5×10^{6}	38×10^{-9}

from being the case. It is true that Lord Kelvin does not push his method to the extreme to which I have carried it, but that he uses it only to obtain a general estimate of the *order* of magnitude of a molecule. I have chosen to extend the method, in order that its limitations may appear more clearly.

Quincke's Determination of the Range of Molecular Attraction.—M. Plateau has described Quincke's "wedge method" very clearly, and I will quote the description of it that he gives: † "When a liquid lies against a solid vertical wall that it does not wet, it makes with this wall an angle whose magnitude depends, as is well known, both on the

* For the values of m, see Appendix.

† *Statique Expérimentale et Théorique des Liquides, etc.*, Vol. I, page 211.

nature of the solid and on that of the liquid. This being granted, let us conceive that upon one of the faces of a glass plate there is deposited a wedge-like layer (as the author calls it) of some other solid substance, the edge of the wedge being vertical, and its thickness, exceedingly small near this edge, increasing uniformly and by insensible gradations as we pass away from it. If a liquid is now allowed to rest against the plate so as to touch the glass along part of its boundary and the wedge-shaped layer at some other part, the angle of contact that the liquid makes with the plate will vary as we pass away from the edge of the wedge; for in the neighborhood of this edge the mutual molecular action between the glass and the liquid will still make itself felt. But after we have reached the distance at which the thickness of the wedge becomes equal to the radius beyond which this mutual action is insensible, the angle of contact will become constant, as it will no longer depend upon anything but the mutual action between the liquid and the substance of which the wedge is composed. M. Quincke has succeeded in obtaining, upon glass, wedge-shaped layers of different substances, and he has determined, in each case, the thickness that fulfills the condition indicated. With a wedge of metallic silver, the liquid being water, he has found $l > .0000054$ cm., l being the thickness in question; with a wedge of sulphide of silver, and mercury as the liquid, he found $l = .0000048$ cm.; with mercury and a wedge of iodide of silver, $l = .0000059$ cm.; and with mercury and a wedge of collodion, $l < .0000080$ cm. M. Quincke concludes from his experiments that one may adopt, as the mean value of the radius of sensible molecular attraction in these cases, $l = .0000050$ cm."

Other Methods of Investigation. — Many other ingenious methods have been devised for determining the sizes of molecules and the radius of sensible molecular attraction, but I can consider only a few of them. First of all, we must not omit to mention the result obtained by Plateau himself. He

found, from a study of soap-bubbles, that the limiting thickness of a film of his glycerine liquid — that is, the thickness at which the film becomes unstable — is about .0000114 cm.; and as he believed that the film would be unstable when its thickness was reduced to twice the radius of sensible molecular attraction, he concluded that the value of this radius, in the liquid composing his bubbles, was .0000057 cm. Maxwell, however, has endeavored to show that a liquid film is stable until its thickness is reduced, not to *double* the radius of attraction, but *to that radius itself*. If his theory is correct, we must conclude from Plateau's data that the radius of sensible attraction, in the glycerine liquid, is .0000114 cm. More recently the limiting thickness of soap-films has been accurately measured by Reinold and Rücker, who find it to be about .0000012 cm. Oberbeck found that a coating of metal .0000003 cm. thick is sufficient to polarize platinum — that is, this thickness is sufficient to alter the character of the surface of platinum so that a distinct difference in electrical potential is observed between a plate so prepared and another plate of the pure metal. Lord Kelvin found that "a quite infinitesimal whiff of iodine vapor" is sufficient to alter the surface of a silver plate so that a difference in potential is observable; but I do not know that he has given any numerical estimate of the thickness of the resulting film of iodide of silver. Wiener found that a film of silver .00000002 cm. thick produces a sensible effect on the phase of reflected light. He also found that when a silver plate is reduced in thickness to .0000012 cm., it no longer produces the same effect on the phase of reflected light that a thick plate does. There is no very close agreement among these various results, nor could we reasonably expect that there would be, when the quantities measured are so imperfectly defined, and the methods and substances used are so different. Nevertheless, the results are all of the same general *order* of magnitude, and when taken in connection with those obtained by the methods that I have already described, they suffice to

give us a very good general idea of the sizes of molecules, and of the distance at which molecular forces cease to be sensible.

Number of Molecules in a Unit Volume of Gas.—According to Avogadro's law, all gases contain the same number of molecules per unit volume, when they are subject to the same conditions; and it will be interesting to calculate this number for some given temperature and pressure. If we continue to regard the molecules of a gas as spherical, the volume of a single molecule is $\frac{1}{6}\pi\delta^3$; and if N is the number of them in a cubic centimeter of the gas, the combined volume of all the molecules in this cubic centimeter will be $\frac{1}{6}N\pi\delta^3$. But this is what we have called the "aggregate molecular volume," and have denoted by ϵ. Hence

$$\epsilon = \frac{1}{6}N\pi\delta^3, \text{ or } N = \frac{6\epsilon}{\pi\delta^3}. \tag{55}$$

By substituting in this equation the values of ϵ and δ that we have found for various gases, we obtain the values of N given in the table.

NUMBER OF MOLECULES IN A UNIT VOLUME OF GAS, AT 0° C., AND ATMOSPHERIC PRESSURE.

GAS.	NUMBER OF MOLECULES.	
	In a Cubic Centimeter.	In a Cubic Inch.
Hydrogen	6.1×10^{18}	95×10^{18}
Nitrogen	5.5×10^{18}	86×10^{18}
Oxygen	6.2×10^{18}	97×10^{18}
Carbon dioxide	23.2×10^{18}	363×10^{18}

These numbers are as nearly equal as could well be expected. It must be remembered that in the determination of N we have the accumulated effects of all the errors that have been

committed in obtaining the coefficients of viscosity, the free paths, the "aggregate molecular volumes," and the molecular diameters. The values of N for hydrogen, nitrogen, and oxygen agree among themselves remarkably, but the value for carbon dioxide is apparently too large. You will observe that in determining ϵ I have used Mr. Sutherland's data for the first three gases, and Clausius's data for the last one. If we take Mr. Sutherland's results for *all* the gases, we should have, for carbon dioxide, $\epsilon = .00117$,* which is about sixty per cent greater than the value given by Clausius's equation (30). By using Mr. Sutherland's value of ϵ in equation (53) we find $\delta = 63 \times 10^{-9}$ cm.; and a further substitution, in (55), gives $N = 8.9 \times 10^{18}$ as the number of molecules in a cubic centimeter of the gas, under the stated conditions. This agrees much better with the results given in the table for hydrogen, nitrogen, and oxygen; and, as these four values of N have been deduced from *independent* observations, I think we may reasonably conclude that Clausius's theorem will give us a fairly accurate knowledge of molecular diameters, and hence also of N, when the mathematical investigation of the kinetic theory of gases has been carried far enough to enable us to construct a theoretically perfect gas equation, from which to deduce accurate values of ϵ. At present I think we can only say that at 0° C. and under one atmosphere pressure, one cubic centimeter of gas contains something like 7,000,000,000,000,000,000 molecules. This corresponds to about 110,000,000,000,000,000,000 per cubic inch.

Illustrations of Molecular Magnitudes.—I have given you a lot of numbers with strings of ciphers attached to them, sometimes running away off to the right, and at other times off to the left. I should like, now, to give you a few homely

* See the *Philosophical Magazine* for March, 1893, page 232. The quantity that I have denoted by ϵ is found by dividing Mr. Sutherland's β by the volume of a gramme of the corresponding gas, measured at 0° C. and one atmosphere, and taking $\frac{4}{5}$ of the quotient. In the case of CO_2 we have $\epsilon = \frac{4}{5} \times (0.692 \div 505) = .00117$.

illustrations of what these numbers mean. We have found that in gaseous bodies the molecules are moving with speeds comparable with that of a cannon ball — indeed, we found that the average velocity of a hydrogen molecule, at 0° C., materially exceeds a mile a second, which speed has never been attained with the best modern artillery. We have found that the average distance that a gas-molecule travels, under ordinary circumstances, between successive collisions with its fellows, is only a few millionths of an inch, — a distance far too small to be seen with certainty even by the most powerful microscopes. The number of collisions experienced by a single molecule of gas in one second was also found to be very great. Every nitrogen molecule, for example, is struck by its fellows, under the standard conditions, something over 5,000,000,000 times per second. It would take you fifty-three years to count that many, if you should count three every second, and twenty-four hours every day. We have found that molecules are amazingly small — so small, for example, that if every man, woman, and child in this world were to lay down a molecule of carbon dioxide so that all these molecules should lie in a straight line, and each should touch its neighbors, the row thus formed would hardly be more than a yard long.* A cube formed of a hundred thousand million molecules of hydrogen in contact with one another would hardly be visible in the finest microscopes that we have. The number of molecules in a cubic inch of gas at the freezing point and under atmospheric pressure is so great, that notwithstanding the fact that it would take about 55,000,000 hydrogen molecules to make a row one inch long, and that only one three-thousandth of the volume of the gas is really filled by matter (the rest being vacuous space around the molecules), if all the molecules that exist in a cubic inch of this gas were placed in a row, touching one another, they would form a line about 32,000,000 miles long, or long enough

* According to the *Statesman's Year-Book*, the population of the world, in 1890, was about 1,468,000,000.

to wind around the earth more than a thousand times. If the molecules contained in a cube whose edge is *one inch and a half* were similarly arranged, they would reach from the earth to the sun. To state the same thing in still another way, let me say that if the molecules in a cubic inch of gas (under the assumed conditions of temperature and pressure) were spread out uniformly so as to form a single sheet or layer, and if they were distributed so that their average distance from center to center was about the same as the corresponding distance between the letters on this page, then the layer in question would cover all the six continents of the earth, six times over. It would be easy to investigate the speed of rotation of molecules in gases, by the aid of Boltzmann's theorem, and to show, by making certain assumptions about their shapes, that hydrogen molecules (for example) rotate so swiftly that they perform one entire revolution while light, with its prodigious velocity of 186,000 miles per second, is traveling a few millionths of an inch. It might also be interesting to speculate on the tensile strength of a substance that could hold together while rotating with so fearful a speed. I have not discussed these points, however, for I was afraid that if I should do so, I could not help conveying the impression that we know far more about them than we do. Some day it may be profitable to theorize about these things, but certainly the time is not yet come.

VI. THE CONSTITUTION OF MOLECULES.

Preliminary Remarks. — We are now about to leave the field of knowledge altogether, and to enter the vast domain of speculation; for I think I can safely say that at present we do not possess the least particle of positive information concerning the constitution of molecules. I have even had doubts about the propriety of discussing the subject at all, so profound is our ignorance of it; but upon more mature reflection it seemed hardly proper to omit all mention of the

views that have been advanced by physicists from time to time, especially as we have made certain tacit assumptions about the constitution of molecules in the preceding sections — assumptions whose uncertainty should at least be pointed out. The chief difficulty before the philosopher who would investigate the structure of molecules lies in the fact that it is impossible to see or measure a molecule directly. We know them, not individually, but only in the aggregate; and we can infer their structure only by observing the gross results of their interaction in large numbers. Our situation may be best illustrated, perhaps, by imagining a huge being who could observe only the general trend of events upon the earth — the march of civilization and the rise and fall of empires — and who desired to infer from these data the anatomy and mental characteristics of the invisible creatures whose individual acts, when summed up, had given rise to these phenomena. It is obvious that in either case the problem is of enormous difficulty, and that, to a certain extent, it may prove to be indeterminate. We must proceed by making various assumptions about the constitution of molecules, and we must then rigorously follow out the results of these assumptions and compare them with the facts. Those that are found to disagree with the facts will then be rejected, and the others will be tentatively retained until new and crucial facts may be discovered, which shall make a further rejection possible. By such a process of exclusion we may hope to arrive, some day, at a fair knowledge of the structure of molecules; but the progress of the molecular theory in this direction is likely to be extremely slow, on account of the mathematical difficulties that continually present themselves, and which can be overcome only by a great amount of patient labor.

General Facts to be Explained. — The successful molecular theory — or "final theory," as we may call it, — must explain a vast range of phenomena, extending all the way from those

that thrust themselves upon us in our everyday life to those more recondite ones that can be observed only in the laboratory, under specially favorable conditions. Some physicists demand that the final theory shall explain even the *inertia* of matter; but it seems to me that this is asking too much, and that such a demand implies an imperfect understanding of what "explanation" means. To "explain" a fact is to show that it is a necessary consequence of other facts that are more readily grasped by the human understanding; and as inertia is perhaps the most fundamental of the known properties of matter, it seems as though any attempted explanation of it would only involve us in a sea of words and ink, without enlightening us in the least. Elasticity, however, is certainly capable of explanation. When it is manifested by bodies of sensible size, we refer it to the interaction of the molecules of which the bodies are composed; but when it is manifested by the molecules themselves, some further explanation is required. I have told you that molecules are perfectly elastic; but I have merely postulated the elasticity, and have not attempted to explain it. We shall see, presently, that Lord Kelvin's vortex theory affords a mechanical explanation of the elasticity of molecules, and although I should not like to say that his explanation is the correct one, it proves to us, at least, that such an explanation is possible. The final molecular theory must unravel the mysteries of chemical and physical *attraction*, and must also show why an atom of *A* has a powerful affinity for an atom of *B*, but is comparatively indifferent towards an atom of *C*. It must unify the conceptions of chemistry and physics, and consolidate these sciences into one grand Science of Matter. It will also have to explain the possibility of such enormous and comparatively stable aggregates of atoms as occur in proteid bodies and gums, whose molecular weights, in some instances, are believed to be as high as 13,000 or 14,000. These are formidable things to require of an infant theory, and yet no theory which does not cover them all can possibly hope for final acceptance. It may be well to indicate

some of the general facts of chemistry and physics that are likely to serve as stepping-stones towards the great theory of matter that future generations will undoubtedly evolve, and I shall therefore refer briefly to Dulong and Petit's law, to Prout's hypothesis, to the periodic law of Mendeleieff and Meyer, and to the theory of radiation.

Dulong and Petit's Law. — In the early part of the present century two distinguished French physicists, MM. Dulong and Petit, announced that the specific heats of certain elements upon which they had experimented are inversely proportional to the respective atomic weights of those elements, and from this they concluded that the amount of heat required to raise the temperature of N atoms by 1° is the same for all the elementary bodies. This remarkable generalization did not meet with universal and immediate acceptance, because it failed in numerous cases unless the atomic weights of the corresponding elements were changed somewhat from the values that had been assigned to them from purely chemical considerations. Moreover, it could not possibly be an *exact* law, because the specific heats of bodies are not constant, but vary with the temperature, and sometimes to a considerable extent. Subsequent experimenters have paid great attention to Dulong and Petit's law, however, and now that the atomic weights of the more familiar elements have been pretty well determined, the law is found to be surprisingly near the truth. Dr. L. Meyer gives a list of fifty elements which accord with it very well, and I have selected ten of them, almost at random, to show you its wide applicability, and the order of its accuracy.* The atomic weights in these elements range from 7 to 240, and yet when we multiply each of them by the corresponding specific heat we find that the product remains constant, or nearly so. Furthermore, the small variations that do occur do not appear

* Dr. Lothar Meyer, *Modern Theories of Chemistry* (London, Longmans, Green & Company, 1888), page 73.

to follow any particular law, but have rather the character of "errors of observation"; and although they are quite too large to be attributed to this cause, their irregularity forces

ILLUSTRATIONS OF DULONG AND PETIT'S LAW.

ELEMENT.	ATOMIC WEIGHT.	SPECIFIC HEAT.	PRODUCT.	ELEMENT.	ATOMIC WEIGHT.	SPECIFIC HEAT.	PRODUCT.
Lithium . . .	7.0	.941	6.6	Antimony . .	120	.0508	6.1
Aluminium . .	27.0	.214	5.8	Tungsten . .	184	.0334	6.1
Potassium . .	39.0	.166	6.5	Gold . . .	196	.0324	6.4
Copper . . .	63.2	.0952	6.0	Bismuth . .	207	.0308	6.4
Silver . . .	107.7	.0570	6.1	Uranium . .	240	.0277	6.6

upon us the conviction that Dulong and Petit's law is not a mere "first approximation" to the relation between specific heat and atomic weight, but that it expresses that relation accurately, and that the outstanding differences are due to causes which are not functions of the atomic weights alone. Dulong and Petit's law has been thought, by some, to indicate that matter, in the last analysis, is of only one kind. To my own mind the law seems to controvert this hypothesis, rather than to sustain it; for if there is really but one ultimate kind of matter, we might indeed expect to find the specific heats of bodies equal, but I think we should hardly look for them to be inversely proportional to the molecular weight. Dulong and Petit's law seems rather to be an experimental indication that some modification of Boltzmann's law of the partition of kinetic energy in the molecules of gases will also be found to be true of the molecules of liquids and solids. To illustrate, let us consider a gas in which the effects of intermolecular attraction are insensible. Maxwell has shown that if two such gases have the same temperature, their kinetic energies of translation (per molecule) will also be equal [page 35]. Since this is true for *any* temperature, it follows that if the two gases be raised through the same *range* of temperature

(say from t_1 to t_2), the *increase* in the average kinetic energy of translation will be the same in each case. For the sake of clearness let us name the two gases "A" and "B," respectively; and let us denote by k the average increase in kinetic energy of translation experienced by a molecule of either gas when the temperature is raised from $t°$ to $(t+1)°$. Now if n_1 and n_2 are the number of degrees of freedom of the molecules of A and B, respectively, then the total increase in kinetic energy of N molecules, when the temperature is raised from $t°$ to $(t+1)°$, will be

$$\frac{n_1}{3} \cdot Nk \text{ and } \frac{n_2}{3} \cdot Nk,$$

respectively. But since we assume that the change in potential energy is insensible, it follows that these quantities are equal to $s_1 W_1$ and $s_2 W_2$, respectively, where s is the specific heat of the gas, and W is the weight of N molecules. Hence,

$$\tfrac{1}{3} n_1 Nk = s_1 W_1, \text{ and } \tfrac{1}{3} n_2 Nk = s_2 W_2. \tag{56}$$

Now although we do not know N with any considerable approach to accuracy, we do know that

$$W_1 = Nw_1 \text{ and } W_2 = Nw_2,$$

where w_1 and w_2 are the weights of a molecule of A and B, respectively. Substituting these values of W_1 and W_2 in (56) and dividing by N, we have

$$\tfrac{1}{3} n_1 k = s_1 w_1 \text{ and } \tfrac{1}{3} n_2 k = s_2 w_2.$$

Hence, finally,

$$\frac{s_1 w_1}{n_1} = \frac{s_2 w_2}{n_2}; \tag{57}$$

and this, I imagine, is the true form of Dulong and Petit's law. As the absolute values of w are not known with precision, we may advantageously use, instead of them, those relative values which chemists call the "molecular weights." Equation (57) may be written

$$sw = Cn, \tag{58}$$

where s represents specific heat, w represents molecular weight, n is the number of degrees of freedom of a molecule, and C is a constant. You will notice that this differs from Dulong and Petit's law, as ordinarily stated, in the introduction of n in the second member. It may be interesting to determine C by examining some of those gases and vapors for which n has been determined by means of equation (22).

DETERMINATION OF C.

SUBSTANCE.	SPECIFIC HEAT.	MOLECULAR WEIGHT.	PRODUCT.	n.	C.
Mercury vapor	.015	200	3.00	3	1.00
Hydrogen	2.43	2	4.86	5	.97
Oxygen	.154	32	4.93	5	.99
Nitrogen	.173	28	4.84	5	.97
Carbon monoxide	.173	28	4.84	5	.97
Hydrochloric acid vapor .	.132	36	4.75	5	.95
Water vapor	.371	18	6.68	6	1.11
Carbon dioxide	.15	44	6.60	7	.94

The average of these values of C is 0.98; but 0.98 is so near to 1.00 that the data that we have are not sufficient to distinguish between the two with certainty. We may therefore consider C to be unity, and may write equation (58) thus:

$$sw = n. \tag{59}$$

Now if some law closely analogous to Boltzmann's holds true for *solids*, then Dulong and Petit's law might follow as a natural consequence. If we strain the point a little and apply Boltzmann's law itself to solids, we see that the constancy of the product of the specific heat and molecular weight would merely imply that the molecules of the substances under discussion have the same number of degrees of freedom. We could even deduce the number of degrees of

freedom in any given case, by substituting in (59) the proper values of s and w, remembering (in case the body is an element) that w is the *molecular* weight, and not the *atomic* weight. The elements in Meyer's list would then appear to consist, for the most part, of molecules having 11, 12, or 13 degrees of freedom. Of course the explanation of Dulong and Petit's law that I am offering you is merely speculative at present; but if it be accepted for the moment, then certain of the difficulties that beset other explanations of the law disappear. For example, it is probable, beforehand, that the molecules of all bodies do not have the same number of degrees of freedom; and hence, in accordance with (59), we could not reasonably expect the product of the specific heat and the molecular weight to be always the same, but should rather expect that bodies would be divisible into *classes* in this respect, the product being the same throughout any one class, but different in different classes; and this is the fact, provided the law be extended (as I think it should be) so as to include compounds.* Again, we can understand why the law is not exact; for Boltzmann's theorem (and presumably its analogue for solids also) relates only to the partition of *kinetic* energy among the various degrees of freedom of the molecules. The law of distribution of *potential* energy is doubtless quite different; and as the specific heat of a body corresponds to the increase in its *total* energy, it follows that (59) will not be strictly true. The wide divergence from Dulong and Petit's law exhibited by certain bodies (such as boron) at some temperatures, and the comparatively good agreement of these bodies with it at other temperatures, may be due either to a change in the number of degrees of freedom of the molecule, or to a local variation in potential energy great enough to mask the effects of the equable distribution of kinetic energy.

* Of course numerous attempts to so extend it have been made already; but so far as I know, they have not been based on the considerations here presented.

Prout's Hypothesis. — The idea that matter is not really of seventy kinds or so, but that it consists of only one fundamental kind, is quite ancient; but "in 1815, soon after Dalton's atomic theory had met with general recognition, Prout brought forward the view that the primordial matter of which all elements are composed is *hydrogen*, and that consequently the atomic weights of all the other elements are simple multiples of the atomic weight" of that substance.* This hypothesis has provoked much discussion, and since it was first proposed it has been attacked and defended by many distinguished chemists; and although it is rather in disfavor at present, I think we cannot yet say that it has been finally laid to rest. One can hardly glance at a table of atomic weights without being impressed by the close approach of these quantities to integral values. Of course there are conspicuous exceptions — chlorine, for example, — to Prout's hypothesis in its original form, and to reconcile these it has been assumed that the various elements are composed, not of hydrogen, but of some unknown and still simpler substance whose atomic weight is ½ or ¼ that of hydrogen; but this seems like a very artificial extension of the hypothesis, because by a further extension of the same kind we could easily account for any exceptions whatever. The fact that many of the atomic weights are *nearly* integral demands some sort of an explanation, however, for it can hardly be accidental. When chemical science was in a less developed condition it was easy to believe that the atomic weight of nitrogen (for example) is 14.00, instead of 14.02 as indicated by experiment, and that the atomic weight of carbon is 12.00 instead of 11.97; but we can no longer entertain any such hypothesis. This point was strongly emphasized by Stas's magnificent researches, for his results are apparently of such extraordinary accuracy that an error of one-tenth of one per cent is quite out of the question in them. "It is possible," says Dr. Lothar Meyer, "that the atoms of all or many of the

* Meyer, *Modern Theories of Chemistry*, page 113.

elements chiefly consist of smaller particles of matter of one distinct primordial form, perhaps hydrogen, and that the weights of the atoms do not bear a simple relation to one another because the atoms contain, in addition to the particles of this primordial matter, varying quantities of the matter which fills space and is known as the luminiferous ether, which is perhaps not quite devoid of weight. This appears to be the only permissible hypothesis." Dr. Meyer's surmise may possibly be correct, although certain grave difficulties would have to be overcome before we could accept it. If you will bear in mind what I said a few moments ago about all these points being purely speculative, I will offer another hypothesis which may not be better than Dr. Meyer's, but which appears to be at least as good, and quite as defensible. There is no harm in letting one's fancy loose in this way, any more than there is in reading a fairy tale; but it is of the first importance, in either case, that we should carefully remember what we are doing, so that *possibility* may not be confused with *probability*. There is one point which is everywhere taken to be self-evident by writers on chemistry, but which is not so, to me, by any means. I cannot see what warrant there is for assuming that when an atom whose weight is A combines with another atom whose weight is B, the weight of the resulting molecule is universally and necessarily $A+B$. This principle, instead of being a truism, must receive a most exact explanation by the final molecular theory. It appears to be true in such reactions as we can observe, but as we have never split an element up into its constituent hydrogen-atoms (if indeed it contains such atoms!) there is no evidence that in such a case the "law of conservation of weight" would still hold true. When we know more about the nature of gravitation we shall be in a better position to discuss this point; but at present I think we may say that it is just *possible* that there may be cases in which an atom of weight A, when combining with another of weight B, does *not* produce a molecule of weight $A+B$. I am well aware that this would make

perpetual motion possible, for if the weight of the given substances happened to be *greater* in the combined state than in the uncombined one, we should only have to let them fall some convenient distance while they are combined, and raise them again while they are uncombined, and we should gain a little energy every time the cycle was repeated; while if combination should cause a *loss* of weight instead of a gain, we could attain the same end by performing the cycle in the opposite direction. Now I am sure that nobody has greater faith in the conservation of energy than I have, and yet we should remember that that grand principle, the discovery of which will cause the nineteenth century to be remembered forever, is nevertheless merely an abstraction from our *experience;* and that it teaches us nothing except that we have never *known* energy to be created or destroyed, and that *with the means at our command* we cannot create it nor destroy it. If it be true, therefore, that matter is composed of some fundamental substance combined with itself in varying degrees of complexity, then whenever the law of conservation of weight would be violated upon splitting a body up into its constituents, or in forming it from them, the means at our disposal can never enable us to effect either the separation or the combination; and so far as we are concerned, such a body would forever remain an element. On the other hand, whenever the law of conservation of weight would *not* be violated upon splitting a body up, the body in question is not an element, but a *compound;* and we can reasonably hope to effect its separation into two or more simpler bodies. This hypothesis explains both the existence of "elements," and the slight deviations from integral values that we find in their atomic weights. I offer it for what it is worth, and have nothing further to say in defense of it.

Periodic Law of Meyer and Mendeleieff. — It has long been known that certain approximate numerical relations exist among the atomic weights of elements that have similar

properties. For example, if we consider the three closely related elements lithium, sodium, and potassium, we find that the atomic weight of sodium is almost exactly the arithmetic mean between the other two. Thus we have Li = 7.01 and K = 39.02, the mean of which is 23.02; and the atomic weight of sodium is 23.00. Again, in the triad calcium, strontium, and barium, we have Ca = 39.99 and Ba = 136.76, the mean of which is 88.38; and the atomic weight of strontium is 87.37. The triad chlorine, bromine, and iodine, affords another familiar example, for we have Cl = 35.37 and I = 126.56, giving a mean of 80.96; and the atomic weight of bromine is 79.77. As I have said, these peculiarities, and numerous other similar ones, were known many years ago; but we are still ignorant of their true meaning. In recent years a great multitude of relations of this sort among the elements have been brought to light, and two distinguished chemists, one a Russian and the other a German, have shown, by independent investigations, that if the elements are arranged in the order of their atomic weights, many of their properties recur, at intervals, in a sort of "periodic" manner, as we pass from one end of the array to the other. Tables have also been prepared, in which the elements are arranged in rows and columns in such a manner that their relations to one another can be plainly seen. I shall not dwell at length upon this "periodic law," because an adequate discussion of it would require a great deal of time. It has been set forth very simply and clearly, however, and also in considerable detail, in Meyer's *Modern Theories of Chemistry*, and in Mendeleieff's *Principles of Chemistry*. When the attempt was made to arrange the elements in *tabular* form, it was found necessary to leave certain spaces in the table vacant. It was easy to imagine that elements would some day be found, which would fit into these spaces; but it was much more difficult to predict the *exact properties* that these hypothetical elements would have. Nevertheless, Mendeleieff undertook the task, and in several instances his predictions

have been fully verified by subsequent discovery. One of the most striking instances of such verification is afforded by the metal known as scandium. Mendeleieff's predictions, and the actual facts as they were afterwards discovered, are here presented in parallel columns, and you will see that the correspondence is extremely close. (The unknown element was provisionally called "eka-boron," from its position in the table of elements.*)

EKA-BORON (*hypothetical*).	SCANDIUM (*actual*).
1. Atomic weight about 44.	1. Atomic weight = 44.
2. Oxide will have formula Eb_2O_3; will be soluble in acids, but insoluble in alkalies; specific gravity about 3.5; analogous to Al_2O_3, but more basic; less basic than MgO.	2. Oxide has formula Sc_2O_3; is soluble in strong acids, but insoluble in alkalies; specific gravity = 3.8; analogous to Al_2O_3, but more decidedly basic.
3. Salts of Eb will be colorless, and will yield gelatinous precipitates with KOH, K_2CO_3, Na_2HPO_4, etc.	3. Solutions of Sc salts are colorless, and yield gelatinous precipitates with KOH, K_2CO_3, and Na_2HPO_4.
4. Sulphate will have the formula $Eb_2 \cdot 3SO_4$, and will form, with K_2SO_4, a double salt which will probably not be isomorphous with the alums.	4. Sulphate has the formula $Sc_2 \cdot 3SO_4$, and forms, with K_2SO_4, the double salt $Sc_2 \cdot 3SO_4 \cdot 3K_2SO_4$, which is not an alum.

There is a certain analogy, historically at least, between this "periodic law" and the rough arithmetical progression known to astronomers as "Bode's law." Bode's law successfully predicted the asteroids, and assigned them their place in the solar system. Afterwards, when Adams and Leverrier undertook their famous labors which ended in the discovery of Neptune, they assumed, naturally enough, that the unknown planet would also conform to the law of Bode, and they arranged their computations accordingly. When the planet had been discovered, and its orbit investigated, it was found to be much nearer the sun than had been anticipated. In

* This parallel-column comparison is from Watt's *Dictionary of Chemistry* (new edition), article *Atomic and Molecular Weights.*

fact, it does not agree with Bode's law at all, and the "law" has therefore been rejected, and is now regarded only as a curiosity. It may be that the "periodic law" of chemistry is destined to a like fate, through the discovery of new elements that cannot be placed in the scheme of classification as it now stands, nor in any modified form of it; yet this is quite improbable, because the periodic law is based on a vast assemblage of facts of different kinds instead of upon a mere observed arithmetical progression, and also because the law is more or less elastic, as will be evident to any one who takes the trouble to look up its history and note the various modifications that it has undergone since it was first proposed. There was nothing elastic about Bode's law, and when the adverse fact came, the "law" gave way before it.

Elastic-Solid Theory of Light. — It has long been known that light is not propagated with infinite rapidity, but that it travels with a finite (though prodigious) speed. It has also been long known that light is not a substance, but that it is a mere periodic disturbance of some kind or other. Now if it be admitted that light is a *disturbance* of some kind, and also that it can travel through all the interstellar spaces of the sidereal universe, it follows that throughout these spaces *there must be some body that is disturbed;* for it would be highly absurd to suppose that a disturbance of any kind could take place in an absolute vacuum. The hypothetical body that is thus assumed to fill all space is called the *luminiferous* (or "light-bearing") *ether.* Of course it is not related in any way to the volatile liquid that chemists know as "ether," and it is unfortunate that the same word should be applied to such different things. The physicists have the right of way here, however, for their ether was discovered and named long before chemists produced the other kind of ether. Although the ether of the physicist does not directly affect our senses in any way, and is quite imperceptible to any chemical or physical tests, its general properties have nevertheless been

deduced (by making certain special assumptions about the nature of light), and, as might be expected, they have been found to be very remarkable. In telling you of them I will outline, in a general way, what is known as the "elastic-solid" theory of light; but I must state, before doing so, that this theory has been recently abandoned and replaced by another one that we shall consider presently. The ether being assumed to fill all space (or to extend, at least, to the most remote visible star), it was conceived, by the advocates of this theory, to be thrown into a state of vibration by the violent movements of the molecules of bodies. If the ethereal vibrations thus set up were comparatively slow, they were believed to produce the phenomena of *radiant heat;* while if they succeeded one another rapidly enough to affect the retina of the eye, they were believed to constitute *light.* The first conclusion with regard to the ether was, therefore, that it is *elastic* in some sense or other; because an inelastic body cannot transmit vibrations. Moreover, since many of the stars that are visible to us are certainly more than a thousand million million miles away, there was good reason for believing not only that the ether is *elastic*, but that it is *perfectly* so. Otherwise the light of the fainter stars would be entirely extinguished by absorption in those tremendous wastes of space. Now an elastic body is something that we know a good deal about, from experience and experiment; and it was therefore easy to investigate the kinds of waves that such a body as the ether can transmit. It was found that such waves would fall into two general classes. In the first place, if the ether were compressible there could be waves of alternate compression and rarefaction; very similar to the sound-waves that we know so well in our own air. Again, if the ether could sustain a *shearing* stress, as solid bodies can, there could be what I may call a wave of propagation of shearing strain. In the first of these cases the to-and-fro displacements of the ether-particles would take place in a direction *parallel* to the direction of propagation of the wave;

and in the second case the displacements would be *perpendicular* to the direction of propagation, just as they are when an undulation travels along a stretched rope or wire. Upon comparing these mathematical results with the facts of nature, it was easily seen, from the phenomena of polarized light, that waves of this second kind do actually occur in the ether; but no phenomena could be discovered which could be attributed to waves of the first kind,* and hence it was concluded that waves of the first kind do not occur. You will see that the reasoning I have indicated leads to the strange results (1) that the ether cannot transmit waves of compression, and that it is therefore probably *absolutely incompressible* (I say *probably,* because the non-existence of waves of compression and rarefaction could also be explained by merely supposing the ether to be devoid of elasticity of volume), and (2) that it can sustain a shearing stress, and is therefore of the nature of an elastic *solid.* Planets, comets, and even such tiny things as atoms, can plunge onward through the ether without experiencing the least retarding effect;† and yet certain kinds of molecular vibration are picked up by it and borne away with prodigious speed into the endless depths of space. The non-resistance offered by the ether is probably due to its *incompressibility,* which property prevents the establishment of a wave of condensation in front of the body, or of rarefaction behind it. There is no friction, and no eddies are produced. The great velocity of ether-waves (186,000 miles a second) shows either that the density of this body is very small, or that its rigidity is very great. Attempts have been made to determine both its rigidity and

* Unless gravitation is such a phenomenon. This point is considered in a subsequent section.

† The retardation experienced by Encke's comet has often been attributed to the resistance of the ether; but as this retardation has been only two-thirds as great, since 1871, as it was in former years, it must be referred to other causes — probably to perturbations from some unknown meteoric stream.

its density, and although no accurate results have been obtained, certain limits have been assigned, within which they are likely to lie. You will find the method of calculation given in Maxwell's article on *Ether* in the *Encyclopædia Britannica.* The minimum limit to the density, as obtained by this method, is 5.36×10^{-19}, the density of water being unity.* Although the ether does not directly retard the motion of material particles, it is undoubtedly influenced by them in some manner. Thus we believe that it penetrates all bodies, and fills up the spaces between their molecules; and as the phenomena of refraction show that the velocity of light is less in a transparent body (say in glass) than it is in a vacuum, it follows that the ether in the glass has either a greater density or a less rigidity than it has in free space. Either of these suppositions will fit the case under consideration very well; but there are other phenomena that will not be satisfied so easily, and it has been found to be impossible to make any single set of consistent assumptions, which shall reconcile the "elastic-solid" theory with the facts. For example, when we come to investigate certain problems in partial reflection from transparent media, and others relating to diffraction from small particles, we are obliged to conclude that it is the *density* of the ether that varies, the rigidity remaining practically constant. On the other hand, the phenomena of double refraction require us to admit that the *rigidity* of the ether in a doubly-refracting body is different in different directions; and hence we conclude that the rigidity of the ether is altered by the presence of molecules of matter — a conclusion at variance with that previously reached by considering the phenomena of diffraction and partial reflection. This is one of the rocks upon which the

* In the article referred to, the density is stated to be 9.36×10^{-19}. This result is erroneous on account of an arithmetical blunder, as any one can easily see by trying to verify Maxwell's computation. Of course the error is of no importance, and I should not have referred to it had I not noticed that whenever the result is quoted, the erroneous value is given.

"elastic-solid" theory went to pieces. There are numerous other objections to it, which are fully as serious as this one. For example, the full mathematical theory of a non-isotropic elastic body involves the consideration of no less than twenty-one coefficients; and if the ether within a doubly-refracting crystal really has different rigidities in different directions, we should expect the phenomena of double-refraction to be much more complex than they really are. In other words, the "elastic-solid" theory is too ponderous. It tends to predict things that do not exist, and in order to prevent it from doing so we have to make certain arbitrary assumptions about the coefficients that occur in the "equations of motion" — a proceeding which is repugnant, I think, to every philosophical mathematician. Taking into account the various difficulties that have arisen in the course of its development, we must admit, with Lord Rayleigh, that "the elastic-solid theory, although valuable as a piece of purely dynamical reasoning, and probably not without mathematical analogy to the truth," is no longer tenable. If we dismiss it from further consideration as being incompetent to explain the entire range of optical facts, of course we are at liberty to form a new conception of the ether also; for the properties that I have already assigned to this body were merely those that the "elastic-solid" theory demanded; and in abandoning that theory we abandon all its consequences at the same time, and prepare ourselves to take a fresh start in a new direction — which direction, fortunately, has already been pointed out.

Electro-Magnetic Theory of Light. — Many years ago Faraday, discussing the supposed phenomena of "action at a distance" as manifested by a magnet, said that he believed that there is some mechanism by which the magnetic influence is enabled to extend itself through a space apparently vacuous. "Such an action," he said, "may be a function of the ether; for it is not unlikely that, if there be an ether, it should have

other uses than simply the conveyance of radiation."* These are profound words — *how* profound they are, it was reserved for Maxwell to show. The old corpuscular theory of light, defended with such ingenuity by Sir Isaac Newton, was thrown overboard long ago because it could not explain the phenomena of interference, and for other reasons that I need not here repeat. Following it came the elastic-solid theory, which we have just considered, and which we have also been obliged to abandon, though perhaps with some reluctance. One would almost be ready to say that the truth *must* lie with one of these two theories, for it would appear that light must be either some kind of a substance, or some kind of a motion in a substance. Undoubtedly this is true, but it now appears that we were thinking of the wrong *kind* of a motion, altogether. Maxwell, after reading Faraday's experimental researches, was so impressed by them and by that marvelous insight into things which seemed, in Faraday, almost like intuition, applied his own ingenious and powerful mind to the problems whose solution Faraday had dimly glimpsed, and succeeded in completely revolutionizing our notions of light, and showing us the whole subject from an entirely new point of view. I shall not attempt to discuss the general theory of electricity, because it would lead us too far away from our subject; but I must indicate, as briefly as I can, the nature of Maxwell's theory of light. He agrees with previous writers that light is some sort of a periodic disturbance in some sort of an ether, and that the displacements that occur as the wave progresses are indeed perpendicular to the direction in which the wave travels; but he teaches us that these displacements are *not* analogous to those that are produced in an elastic-solid when that solid is deformed. He considers that they are of an *electrical* nature, and that we must learn about them, not by observing the behavior of elastic bodies under stress, but by observing the phenomena exhibited by *electrified* bodies; and this, you will see, is an

* *Experimental Researches in Electricity*, Vol. III, p. 331.

entire change of base. Maxwell has given us the fundamental equations that must be satisfied when an electrical wave is propagated through the ether — equations analogous to the "equations of motion" of the old elastic-solid theory — and by means of these equations the entire theory of light can be constructed on the new basis. The theory thus constructed agrees well with the facts of observation, and it is free from the numerous objections that beset the old elastic-solid theory. Moreover, it successfully withstood the searching experimental tests devised by the late Professor Hertz, whose labors have shown us in a very direct manner that electrical radiations are propagated with the same speed as light, and that they can be reflected, refracted, diffracted, polarized, and made to interfere; so that we are now quite ready to admit that light consists in a rapid succession of such radiations. It is not at all essential to Maxwell's theory of light that we should know what an "electrical displacement" really is. We derive his fundamental equations from a study of electrical phenomena as observed in gross matter, and we then apply these equations to the ether, and deduce, by means of them, the laws that govern the propagation of electrical disturbances in that body. We then observe that the laws so deduced are precisely the same as those that have long been known to hold true for *light;* and hence we conclude that light is an electrical phenomenon. This is the whole story, so far as we have any positive *knowledge* of it at present. We have some dim *ideas* about the nature of electric and magnetic displacements, but I think it is safe to say that we know little or nothing about them that is not liable to be profoundly modified by subsequent research. It is quite probable that there is some kind of an ethereal *rotation* going on in a magnetic field, because it is hard to account for magnetic rotation of the plane of polarization on any other hypothesis. However, it should be remembered that even this assumption is by no means beyond controversy, for the plane of polarization of light is affected by magnetism *only*

when molecules of gross matter are present. There is a great deal of work to be done before we can form a clear and true conception of the ether, and of what goes on in it in the vicinity of an electrified body, or a magnet, or a ray of light;* but when such a conception has been attained, we shall incidentally learn a great deal about the relation of ether to matter, and about the constitution of the molecules of which matter is composed.

Provisional Assumptions about the Constitution of Molecules. — In discussing the molecular theory of matter I have made certain assumptions about the constitution of molecules, which are perhaps the most natural ones to make, and which ought therefore to serve as a basis for our investigations, at least until it appears that they are inadequate, or that some other assumptions would be better. Thus I have assumed that molecules are composed of smaller bodies called atoms, which are held together (but not necessarily in *contact*) by certain attractive forces, whose precise nature we have not determined. The atoms have been assumed, furthermore, to have definite forms and sizes, to be perfectly elastic, and to be subject to the same laws of mechanics that govern the larger masses of matter that we can observe directly. These assumptions are simple enough, but it is far from certain that they correspond with the facts; and at all events they are open to certain grave philosophical objections which we shall presently consider, in connection with Lord Kelvin's vortex-theory. The attractive forces that undoubtedly exist between molecules, must receive some kind of a mechanical explanation, but although some attempts have been made to provide such

* Dr. Oliver J. Lodge's *Modern Views of Electricity* (Macmillan & Co., 1889) is an excellent book on this subject, though I fear that his ingenious models tend to give students a too mechanical conception of the ether and of electric action, and to deceive them into the belief that we know much more about these things than we really do. It is possible, however, that I am too conservative on this point.

an explanation, the subject is still quite obscure.* These forces are sometimes thought to be of an electrical nature; but until we know more about the ether and the mechanism of electric attraction such an assumption can hardly be considered satisfactory. The *elasticity* of molecules certainly admits of explanation, and something has already been done in this direction, as we shall presently see. It is far from certain that molecules even have *definite dimensions;* for they may be mere centers of condensation of the ether, or of some non-ethereal substance distributed through it, and they may be as indefinite in their boundaries as the nebulæ that we see in the heavens. We do not even know that those general principles of mechanics that we call "axioms," and which are derived from our observation of vast aggregates of molecules, are applicable, without modification, to the molecules themselves; and yet I think it is logical for us to adopt them until it can be shown that they lead to false results. So far as the general assumptions that I have made this evening are concerned, I think it can be said that there is no gross failure in the molecular theory that can be attributed to them. The present fragmentary state of the theory appears to be attributable to the enormous mathematical difficulties that are involved, rather than to error in the premises. As I have told you, the assumptions that we have made are liable to certain philosophical objections, and for this reason we must consider them to be merely *provisional,* accepted for the present as convenient stepping stones, but subject to revision as the growth of the molecular theory proceeds. We are not yet prepared to develop the molecular theory from any point of view that differs materially from that which I have given you, but it will be interesting to note the direction in which future research is likely to lead us, and for this reason I must notice two or three of the more important hypotheses that have been advanced, concerning the constitution of molecules.

* Some of these attempts are considered in a subsequent section on "Gravitation."

Rankine's Hypothesis.—I do not quite know what I ought to say about Rankine's views concerning the constitution of molecules. He certainly did deduce many of the known properties of bodies from his "hypothesis of molecular vortices," but I am not aware that any other mathematician has found that hypothesis promising enough to call for further investigation. He attributes the hypothesis to Sir Humphrey Davy, but it has long been known by Rankine's name because he was the first to develop it by mathematical methods. The hypothesis of molecular vortices assumes "that each atom of matter consists of a nucleus or central point enveloped by an elastic atmosphere, which is retained in its position by attractive forces, and that the elasticity due to heat arises from the centrifugal force of those atmospheres, revolving or oscillating about their nuclei or central points."* He does not attempt to decide "whether the elastic atmospheres are continuous, or consist of discrete particles"; nor did he find it necessary to determine whether the nucleus of a molecule "is a real nucleus having a nature distinct from that of the atmosphere, or a portion of the atmosphere in a highly condensed state, or merely a center of condensation of the atmosphere, and of resultant attractive and repulsive forces." He believed "that the vibration which, according to the undulatory hypothesis, constitutes radiant light and heat, is a motion of the atomic nuclei or centers, and is propagated by means of their mutual attractions and repulsions." This form of the theory of light receives some considerable support from the phenomena of double refraction and polarization, but of course it has no bearing on the mode of propagation of light through *free space,* unless the ether itself is conceived to have a similar constitution. Rankine perceived this fact very clearly, and in an interesting paper on light, read before the British Association in 1853,† he

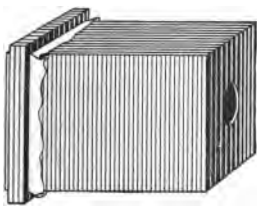
* Rankine, *Miscellaneous Scientific Papers* (London, Charles Griffin & Co., 1881), page 17.

† *Miscellaneous Scientific Papers*, page 156.

assumes "that the luminiferous medium is composed of detached atoms or nuclei distributed throughout all space, and endowed with a peculiar species of polarity, in virtue of which three orthogonal axes in each atom tend to place themselves parallel respectively to the corresponding axes in every other atom; and that plane-polarized light consists in a small oscillatory movement of each atom round an axis transverse to the direction of propagation." A serious objection to Rankine's hypothesis of molecular vortices is, that it seems to hold out little promise of eventually offering a mechanical explanation of *attraction.* He merely postulates the attraction, and when we look for some sufficient *cause* for it, the hypothesis is barren, and its prophet dumb. The facts of chemistry are also hard to explain from Rankine's point of view; and if we judge the hypothesis of molecular vortices according to its fruits, we must pronounce it a step in the wrong direction; for it still remains where it was some forty years ago.

Lord Kelvin's Vortex Theory. — We have now to consider a very curious and interesting theory of the constitution of molecules, which was originally proposed by Lord Kelvin. Most of the theories that have been advanced have assumed that there are two kinds of matter, one being that which we ordinarily call "matter," and the other being the imponderable "ether," whose existence we have been obliged to admit in order to account for the phenomena of electricity, light, and radiant heat. Lord Kelvin has dispensed with one of these substances altogether, by assuming that molecules (or the atoms composing them) are merely definite portions of the ether itself, which are distinguished from the remainder of that vast body by being endowed with a peculiar kind of motion, called "vortex motion." I should like to give you a clear idea of vortex motion, and perhaps it will be best for me to begin by calling attention to certain cases of it that you are likely to have seen. The grandest example occurring in

nature is the *cyclone*, which consists, as you know, in a violent rotation of the air about a central vertical axis, accompanied by a translation of the axis in a direction perpendicular to its length. You have probably often seen smoke-rings blown from the stack of a locomotive, and if you have observed them closely you have noticed that they are in rapid rotation, the smoke-particles passing up through the ring on the inside and down again on the outside. These rings are good examples of vortex motion in which the axis of rotation returns into itself so as to form a closed curve. Experienced smokers can often produce similar rings, on a small scale, with their lips; and very good ones can be made by the simple apparatus devised by Professor Tait and shown in Fig. 50. This apparatus consists of a box with a round hole several inches in diameter in one end of it, the other end being removed and replaced by a tense sheet of india rubber.



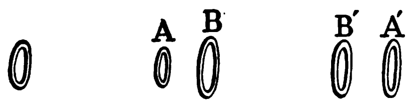


FIG. 50. — TAIT'S APPARATUS FOR PRODUCING SMOKE-RINGS.

In order to make the rings visible, the box may be filled with smoke or some similar substance. Professor Tait, for this purpose, makes use of the dense cloud of sal ammoniac particles that is produced when vapors of ammonia and hydrochloric acid are allowed to mingle with each other. The ammonia is sprinkled over the inside of the box, and the hydrochloric acid is generated by pouring strong sulphuric acid over some salt contained in a saucer which rests upon the bottom of the box. If the stretched sheet of rubber be now gently struck, a beautiful smoke-ring issues from the front of the box. The constitution of the smoke-rings produced in this manner is indicated in Fig. 51, where the small,

curved arrows indicate the direction of the rotation, and the large, straight one shows the direction in which the ring travels.* A great variety of beautiful experiments may be tried by means of this simple apparatus. For example, we may study the action between a pair of rings by producing two of them in quick succession, as shown at A and B, in Fig. 50. When the experiment is successful we shall see the first ring enlarge and slacken its speed of translation, while the second one grows smaller and moves faster, so that it presently passes through the first one, and the rings take the relative positions indicated at B' and A'. The ring A' being now the foremost one, tends to slow down and enlarge, and the ring B' tends to grow smaller and move faster so as to pass through A', and so on perpetually; but it is difficult to realize more than one such passage, in the actual experiment, because the viscosity of the air soon stops the rotation of the ring, and when the rotation has ceased the ring is no longer a vortex, but merely a wreath of smoke. Helmholtz was the first man to investigate vortex motion by rigid mathematical methods, and some of his results are very interesting. In his researches the fluid in which the vortices exist was assumed to be frictionless, homogeneous, and incompressible. These properties being admitted, he showed (1) that a vortex can never be *produced* nor *destroyed* in a medium of this character, so that if such vortices exist, they will continue to exist forever; (2) that a vortex cannot have a free end *within the fluid*, and hence every vortex must either return into itself so as to form a *closed curve* (like a smoke-ring), or be infinite in

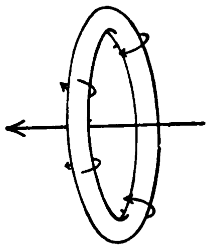


FIG. 51.—DIAGRAM OF A SMOKE-RING.

* It seems hardly necessary to say that the smoke and the sal ammoniac fumes play no part whatever in these experiments, except to make the rings *visible*. The existence of the rings can be demonstrated when the smoke is entirely absent, by the effects produced on a distant sheet of tissue paper, or a candle-flame.

length, or have its ends upon a bounding surface of the fluid; (3) that a vortex always consists of the *same portion of fluid*, so that when it travels through the surrounding fluid it is not alone the *motion* which progresses (as would be the case in a wave); the vortex does not lose its identity, but "moves" in the same sense that a projectile moves when propelled through the air; (4) no two vortices can ever intersect each other, and no vortex can ever intersect itself. It is also known that a vortex in a frictionless, incompressible fluid would behave like a perfectly elastic body. Many other properties of vortices have been deduced, but those that I have mentioned will be sufficient for our present purposes. Some eight years after the publication of Helmholtz's paper on vortex motion, and while watching Professor Tait's beautiful experiments on smoke-rings, Lord Kelvin conceived the idea that atoms may possibly be vortices in the luminiferous ether. There is much to be said in favor of this hypothesis, from a philosophic point of view. As we have seen, it enables us to dispense with one of the two "kinds of matter" entirely, for it teaches that all things are composed primarily of ether, and that "gross matter" is distinguished from the surrounding medium solely by its being endowed with the peculiar kind of motion that we have just been considering. It explains the *permanence* of "gross matter," because Helmholtz's investigations prove that a vortex-atom in a frictionless fluid can never be created nor destroyed. It explains the *elasticity* of molecules, because it shows that an ether-vortex would behave like a perfectly elastic body, even though the ether itself were entirely devoid of elasticity. Most of the theories of matter leave the existence of some 70 or so elements as much of a mystery as the existence of "species" was, in the biological world, before the time of Spencer and Darwin; but the vortex-theory gives us at least a suggestion on this point. I have already told you that a finite vortex, in an infinite, frictionless fluid, *must return into itself;* but there is no reason for assuming that it must form a simple ring, like a

smoke-ring. There is no assignable reason why it could not have the form suggested in Fig. 52, or any other more complicated form; and since a vortex can never intersect itself, the degree of knottedness of a vortex-atom can never change. It may be, therefore, that the elements differ in their properties, on account of their atoms differing in knottedness. The vortex-theory of Lord Kelvin also holds out some faint promise of explaining other facts of chemistry; and in this respect, at least, it is decidedly superior to Rankine's hypothesis.

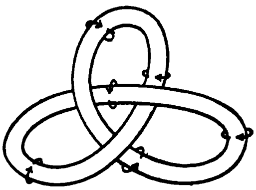


FIG. 52. — A KNOTTED VORTEX.

I will not attempt to say just what explanation of chemical *combination* might prove to be best, but there is a certain suggestiveness in the behavior of a pair of similar and nearly parallel smoke-rings, which tend to thread through and through each other perpetually, as illustrated in Fig. 50. A host of other possibilities lie before the vortex-theory, but it is doubtful if further speculation would be profitable for us. The consequences of the vortex-theory can be deduced by rigid mathematical methods, and it is idle to try and guess them in advance. In fact, one of the greatest philosophical advantages of the vortex-theory is, that it admits of so few assumptions. Other theories are more or less elastic, and can be modified so as to bring them into harmony with each new phenomenon; but when the fundamental assumptions of the vortex-theory have once been made, we are bound to adhere to them, and to deduce from them, by exact analysis, all the known properties of matter. As Maxwell says, "When the vortex-atom is once set in motion, all its properties are absolutely fixed and determined by the laws of motion of the primitive fluid, which are fully expressed in the fundamental equations. The disciple of Lucretius may cut and carve his solid atoms in the hope of getting them to combine into worlds; the follower of Boscovich may imagine new laws of force to meet the requirements of each new phenomenon; but

he who dares to plant his feet in the path opened up by Helmholtz and Thomson [Lord Kelvin] has no such resources. His primitive fluid has no other properties than inertia, invariable density, and perfect mobility, and the method by which the motion of this fluid is to be traced is pure mathematical analysis. The difficulties of this method are enormous, but the glory of surmounting them would be unique."* The vortex-theory is inseparably united to the theory of electricity and light, since both of these theories involve a discussion of the ether; and it remains to be seen whether a constitution can be imagined for that body which shall explain the propagation of radiant energy, without excluding the possibility of vortex-motion. Before the old elastic-solid theory of light was abandoned, the vortex-atom could hardly be seriously considered; for a vortex in an elastic-solid is a manifest absurdity. The electro-magnetic theory cleared the way for the vortex-atom, however, by teaching us that our elastic-solid analogy was erroneous. We are now free to form a new conception of the ether, which may possibly reconcile the vortex-atom with the theory of light; but our past experience in this direction has shown us that we should proceed with extreme caution. The advocates of the vortex-theory are extending their theory to the ether itself, in an attempt to explain how that body may be a frictionless, incompressible fluid, and yet have elasticity. For this purpose the ether is regarded as a perfect snarl of minute, interlacing vortices, which are normally in equilibrium, but which serve as an elastic framework for the transmission of radiant energy. This branch of the vortex-theory is too abstruse and too imperfectly developed to be considered further in this place; and it may be said of the vortex-theory in general, that it is full of enormous mathematical difficulties, and that for this reason we can regard it, at present, only as a highly interesting possibility, whose consequences must be traced out by future generations.

* *Encyclopædia Britannica*, article *Atom.*

Dr. Burton's Strain-Figure Theory. — Numerous other theories of the constitution of molecules have been advanced, but most of them are open to so many objections that they cannot be considered to be tenable at present, and need not be discussed in this place. As an example I may mention the complicated theory of Lindemann, which considers a molecule to consist of a series of concentric spherical shells, each of which is elastically connected with its neighbors. Dr. C. V. Burton's theory must be briefly mentioned, however, for although it is in a very imperfectly developed condition, it presents points of novelty that cannot fail to broaden our conception of what a molecule *may* be.* His theory bears a superficial resemblance to Lord Kelvin's, inasmuch as it considers an atom to consist of a modified portion of the ether; but further than this the two theories are radically different. Dr. Burton conceives that the ether, although possibly of a fluid nature, is nevertheless endowed with *some* sort of elasticity (which is no doubt the case, since otherwise it could not transmit radiant energy). He further assumes that *small* strains in the ether are always proportional to the stresses that accompany them; but that when the strains exceed a certain limit the ether takes a sort of "permanent set," after which it never returns to its primitive condition. Dr. Burton assumes that atoms are merely deformations in the ether that have been produced by such a process of over-straining. Lord Kelvin's vortex-theory has been facetiously called the "doughnut-theory," and perhaps we may designate Dr. Burton's theory, in the same spirit, as the "ether-dent theory"; though neither term is very apt, for a vortex is not necessarily a simple *ring*, and a "strain-figure" in the ether is far from being a mere dent. To give you a clearer idea of Dr. Burton's fundamental assumption I will quote his own description of it. "Consider a region," he says, "either

* For a full account of Dr. Burton's theory see his paper entitled *A Theory Concerning the Constitution of Matter*, in the *Philosophical Magazine* for February, 1892.

infinite or having very distant boundaries, and filled with a homogeneous isotropic elastic medium, whose condition throughout is one of stable equilibrium for small strains of any type. Let the medium now be strained, and held in its strained condition by some compelling agency: there will be a corresponding distribution of stress in the medium, and, provided the strain has at no point too great a value, the original condition will be completely regained after the compelling agency has been removed. But suppose that, instead, the medium is strained further and further from its initial state, and suppose that the restoring stresses do not always increase with the strain, but that beyond a certain point in the process they begin to fall off in value, until at last a point is reached at which the general tendency of the stress is to further increase the strain. If the compelling agency is now withdrawn, the medium will subside into a new condition of stable equilibrium, involving stress and strain at every point. The state of things thus impressed on the medium is, according to my view, an atom or a constituent of an atom; it will hereafter be referred to as a *strain-figure*." This passage does not purport to explain the origin of matter; it is intended merely to convey to the reader the meaning of the term "strain-figure" as used in Dr. Burton's paper. It is suggested, however, that if the ether "had long ago possessed motion of the most general kind, we might imagine its present condition to be due to the degeneration of that motion into a fine-grained turbulence; and if, in the quasi-solid so constituted, the existence of strain-figures were possible, it seems not unlikely that such would incidentally have been formed, unless the motion fulfilled special conditions." If such special conditions were absent, it is therefore possible, on the strain-figure hypothesis, that atoms would have resulted, from time to time, whenever and wherever the motion of the ether should chance to be such as to produce a strain sufficient to give rise to a "permanent set." Dr. Burton's theory, therefore, holds out some hope of even explaining the *origin* of

matter; and in this respect it differs from every other theory with which I am familiar. A mathematical analysis of strain-figures shows that they would possess many of the characteristics that atoms are supposed to have. They could be moved about in the ether without encountering resistance; but we are to consider that when such motion occurs it is not the *ether itself* that moves, but that the modification of structure that constitutes a strain-figure is merely transferred from one part of that body to another part. (The vortex-theory, you will remember, requires us to suppose that an atom always consists of the *same* portion of ether; and in this respect it is diametrically opposed to Dr. Burton's theory.) Gravitation and other inter-molecular and inter-atomic forces are assumed to arise from the distribution of stress that accompanies the strains in the strain-figures. Other consequences of the strain-figure hypothesis have been examined, but the hypothesis is so new and so imperfectly developed that it will hardly be profitable to discuss it further in this place. It is extremely ingenious and interesting, but we must wait for further researches before we can pronounce upon its adequacy or inadequacy.

Internal Vibration of Molecules.—The various phenomena of physics and astronomy compel us to admit that matter can move through the ether freely, without experiencing the least resistance. But since we know that matter can emit radiant energy, it follows that there are modes of molecular motion that *can* be communicated to the ether; and we are impelled to the belief that it is the internal *vibratory* energy that is transmitted in this way. That such energy exists, is quite evident; for if the molecules of bodies are elastic, we must suppose them to be capable of some sort of internal vibration. Let us consider a gas, assuming that its molecules have definite masses and definite sizes, and that for each of them there is a certain shape in which the internal stresses are either zero, or at least a minimum. When two such mole-

cules collide, we must suppose that the collision throws each of them into violent vibration, just as a stretched string is thrown into vibration upon being struck with a hammer. We know that the string can vibrate in different ways: it may vibrate as a whole, or in two equal segments separated by a node, or in three such segments, or four, or, in general, in any number of them. When such a string is struck we usually find that *all* of these possible modes of vibration occur simultaneously, so that the actual motion is very complex. In the stretched string the *periodic times* of the various possible vibrations are proportional to the roots of the equation

$$\sin\left(\frac{\pi}{x}\right)=0;$$

that is, they are inversely proportional to the simple numbers 1, 2, 3, 4, ... Doubtless there is some similar law connecting the periodic times of the possible vibrations that may occur in elastic molecules; though we cannot suppose that law to be as simple as the one connecting the various periodic times of the string. In discussing this question of the vibration-periods of elastic systems, Professor J. J. Thomson tells us that "if the vibrating system . . . were like a bar, the periods would be proportional to the natural numbers for the longitudinal and torsional vibrations," and to the reciprocals of the roots of the equation

$$x\{\epsilon^x+\epsilon^{-x}\}=\pm 2$$

for the transverse vibrations. "If the system were a circular membrane," he continues, "the frequencies would be proportional to the roots of an equation formed by equating a Bessel's function to zero. If the system were a uniform elastic sphere, the frequencies would be the roots of a complicated equation given by Chree in the *Transactions* of the Cambridge Philosophical Society. Other periods which have been worked out are those of circular vortex rings. The

frequencies of the higher vibrations [of such rings] about the circular form are proportional to

$$n\sqrt{n^2-1},$$

where n is a large natural number [*i.e.* integer], and the vibrations about the circular cross-section are proportional to the natural numbers."* We have to think of a gas-molecule as colliding with another one, and then flying off through the ether in a sensibly straight line until it again experiences a collision. At each collision vibrations are set up *within* the molecule, and in the interval between successive collisions — that is, while the molecule is describing its "free path" — it vibrates according to its own proper periods, and the ether in which it is submerged picks up these vibrations and carries them away as radiant heat, or as light. You must not suppose, however, that the process is exactly analogous to what occurs when a particle immersed in a jelly is caused to vibrate. This was indeed believed to be the case when the elastic-solid theory of light was held to be true, but when that theory was discarded it became evident that the real phenomena are essentially different from those suggested by the jelly-analogue; and I think we are still a long way from knowing precisely what *does* take place when a vibrating molecule gives up its energy to the ether. You will observe that writers on the theory of light merely consider what occurs in the ether as it *transmits* the light, and do not attempt to trace the exact processes by which the ethereal motions *originate.* There can be no doubt that here is a fruitful field for investigation, but at present we are hardly prepared to enter upon it. Thus far I have referred only to the vibrations of *gas*-molecules, and I have said that *while a molecule is traversing its free path,* the vibrations that occur are performed in accordance with its natural vibration-periods. At the instant of collision, and for an extremely short time

* Watts's *Dictionary of Chemistry* (new edition), article *Molecular Constitution of Bodies.*

afterwards, the vibrations probably differ more or less from these periods, on account of the extreme violence of the intra-molecular shocks. Careful attention should be paid to this point, since it shows that in solids or liquids, where there is practically *no* free path, and in highly compressed gases where the free path is very short, we cannot expect to find the comparative simplicity of vibration that we do find in gases under ordinary conditions of density. The data for investigating the vibration-periods of molecules are furnished by that simple yet ingenious and powerful instrument known as the *spectroscope*, which enables us to analyze the complicated vibratory motion that they have impressed upon the ether, and to examine separately the constituent simple vibrations of which it is composed. Professor R. C. Kedzie says of this wonderful instrument, "If there was ever a flank movement on nature by which she has been compelled to surrender a part of her secrets it was the discovery of the spectroscope, 'which enables us to peer into the very heart of nature'";* and Maxwell says, though I think his statement is far too strong, "An intelligent student, armed with the calculus and the spectroscope, can hardly fail to discover some important fact about the internal constitution of a molecule." † By the aid of this instrument the vibration-periods of molecules have been patiently studied and tabulated, ‡ and. many attempts have been made to find some relation among them, analogous to the integer-law that holds for stretched strings, and to the other laws that I have told you about in connection with bars and membranes and spheres. No very great success has rewarded these efforts, yet something has been done, and more is sure to follow. Hydrogen, on account of its chemical and physical properties, has long been regarded as a comparatively simple substance; and especial attention has been paid

* *Proceedings of the American Association for the Advancement of Science*, August meeting, 1891, page 162.

† *Nature*, March 11, 1875.

‡ See, for example, Watts's *Index of Spectra* (Manchester, England, Abel Heywood & Son, 1889).

to it on that account, in the hope that the relation among its various vibration-periods might prove to be comparatively simple, and might therefore be the more readily found. Experience has shown that this hope was justifiable; for a remarkable relation among the vibration-periods of hydrogen has been discovered by Balmer. The relation in question is this: If the different lines in the spark-spectrum of hydrogen be numbered consecutively, calling the $H\alpha$ line 3, the next one 4, and so on, then the wave-length of the line whose number is m is

$$\lambda = 3645.42 \frac{m^2}{m^2 - 4}.* \qquad (60)$$

In the following table the results of this formula are compared with the observed facts.

SPARK-SPECTRUM OF HYDROGEN. — BALMER'S LAW.

LINE.	m.	WAVE-LENGTH.		DIFFERENCE.
		CALCULATED.	OBSERVED.	
$H\alpha$	3	6562.8	6563.1	+.3
$H\beta$	4	4860.6	4860.7	+.1
$H\gamma$	5	4339.8	4339.5	−.3
$H\delta$	6	4101.1	4101.2	+.1
$H\epsilon$	.7	3969.5	3969.2	−.3
$H\zeta$.	8	3888.4	3888.1	−.3
$H\eta$	9	3834.8	3834.9	+.1
$H\theta$	10	3797.3	3797.3	.0
$H\iota$	11	3770.0	3769.9	−.1
$H\kappa$	12	3749.6	3750.2	+.6
$H\lambda$	13	3733.8	3734.1	+.3
$H\mu$	14	3721.4	3721.1	−.3
$H\nu$	15	3711.4	3711.2	−.2

* The vibration-period is proportional to the wave-length — being equal, in fact, to the wave-length divided by the velocity of light. Balmer's law can easily be written so as to give the vibration-periods directly; but most writers state it in connection with the *wave-lengths*, and I have thought best to follow the custom thus established.

The agreement between the calculated and observed wave-lengths is very good; and we may conclude that the hydrogen molecule is so constituted that equation (60) represents all the various kinds of elastic vibration that are possible within it, under the conditions that prevail when the spark-spectrum of the gas is being examined. Further than this we cannot go, at present, because no one has shown what sort of a body would have the series of vibration-periods that is represented by (60). I have compared the light-producing vibrations of a molecule to the sound-producing vibrations of a sonorous body; but I must caution you against supposing that there is any very *close* analogy between the two. I have referred to the familiar phenomena of sound, in order to assist your imaginations a little; but you should understand clearly that the ultimate phenomena of light are probably quite different. Since the electrical nature of light has been recognized, the suggestion has been made that molecules behave like conductors in which oscillatory electrical discharges take place, the form, capacity, and resistance of the molecules determining the rapidity of the discharges, and hence also the positions of the spectral lines. I do not think this conception adds much to our knowledge of the molecule, since I can think of an "electrical discharge" only as a motion of some kind, in which the molecule and the ether probably both participate; nor do I think that any other hypothesis is likely to help us much until we have a more exact knowledge of the kind of motion that occurs in the free ether when a ray of light is passing through it. Many physicists appear to regard molecules as aggregates of smaller particles, which are held together by a system of attractive forces, and which execute to-and-fro oscillations of definite periods when the equilibrium of the system is disturbed by a collision, or in any other manner; the light-waves being supposed to arise from these oscillations. Thus Professor J. J. Thomson says that Balmer's law seems to show "that the hydrogen molecule is a system possessing an infinite number of degrees of free-

dom, and not a finite number of rigid particles mutually attracting each other." So far as the to-and-fro theory of the origin of light is concerned, I think we may dismiss it altogether; for we have already assumed that the ether does not absorb energy from a particle moving through it, and it is therefore difficult to conceive how light can be produced by any combination of such to-and-fro motions. Professor Thomson would probably admit this point readily enough, and I am inclined to think that his remark has a deeper significance — that it is aimed, in fact, at Boltzmann's law of the partition of kinetic energy among the different degrees of freedom of gas-molecules; for if that law be true, it follows that the number of degrees of freedom of a molecule is *finite.** For some reason or other Boltzmann's theorem has given rise to a good deal of controversy, and English mathematicians, as a rule, appear to be distinctly hostile to it, although I cannot quite see why. As I understand the theorem, it relates only to the kinetic energy of translation and rotation of the parts of a molecule, and not to those modes of vibration which are analogous to the motions of a sounding wire or bell or other elastic body. The general facts that have been ascertained about the molecules of gases appear to be these: The kinetic energy of the molecules is divisible into two parts, one of which is enormously greater than the other. The greater part consists in various motions of translation and rotation, either of the molecule as a whole or of its parts among themselves; and it is *this* portion of the kinetic energy which is divided up equally among the different "degrees of freedom" of the molecules (using the phrase in its restricted sense). The remaining small part of the total kinetic energy consists in elastic *vibratory* motion, within the very substance of the molecule or its parts; and to this almost infinitesimal portion of the kinetic energy Boltzmann's law does not apply. The motions of translation and rotation are not impeded by the

* See the section on "Generalized Theorems" (page 34), and that on the "Ratio of the Specific Heats of Gases" (page 47).

ether; but the internal *vibratory* motion is of such a character that the ether absorbs it, and bears it away as radiant energy. If a gas receives no heat from without, it will be cooled by the continual abstraction of vibratory energy until its temperature falls to the absolute zero. It is true that only a small part of the total kinetic energy exists at any one time in the form of energy of vibration, but it is also true that the vibratory energy can never entirely disappear while the gas contains any kinetic energy whatever; for *some* vibratory energy must exist, so long as there are molecular collisions. As the vibratory energy is removed by the ether, more will be produced, at the expense of energy of other kinds; and the end of the process will come only when the molecules have all come to rest. If the gas is exposed to radiations emanating from an external heat-source, the phenomena are reversed — the vibratory energy of the molecules increases by absorption of the ethereal vibrations, and the energy so gained becomes presently transformed into energy of other kinds, by means of the collisions that are constantly occurring among the molecules; and when the kinetic energy of translation of the molecules has become sensibly increased by this process, we say that the gas has grown "warmer." The well-known difficulty of heating gases by simple radiation shows, however, that the molecules of these bodies do not readily absorb vibratory energy *from* the ether. I do not know why this is so: solid bodies take up such energy readily enough, and it is not easy to account for the diathermacy of gases. Before leaving this subject I must say that equation (60) is by no means *general*. It applies only to hydrogen, and we cannot, by changing the constants, make it represent the vibration-periods of other bodies. Numerous investigators have sought for similar relations, however, that should hold true for other elements, and with some slight degree of success. Thus Kayser and Runge found that the various wave-lengths of lithium, sodium, potassium, rubidium, and cæsium are expressible by equations of the form

$$\lambda = A + \frac{B}{m^2} + \frac{C}{m^4}.$$

Numerous formulæ of this sort have in fact been proposed, but, so far as I am aware, none of them is as satisfactory as Balmer's. The spectroscope offers us a vast fund of information, and yet for theoretical purposes it is nearly useless, because the key by which the riddle is to be read still remains unfound.

Gravitation. — It is strange that no satisfactory theory of the nature of gravitation has yet been proposed; for the phenomena to be explained are simple, and they are familiar to everybody. The general fact of gravitation is, that between every pair of material particles there exists an attractive force which is proportional to the product of the masses of the two particles, and to the reciprocal of the square of the distance between them. Various attempts to account for this attraction have been made, and although all the theories yet proposed have been eminently unsatisfactory, it may be of interest to review a few of them briefly. Newton naturally gave some attention to the problem, and suggested that the ether is everywhere in a state of pressure, but that for some reason or other this pressure is less in the neighborhood of dense bodies than it is elsewhere. He showed that such a state of things would cause two bodies immersed in the ether to be urged towards each other, and he also showed that if the diminution of pressure at any point, due to the presence of the dense body, were inversely proportional to the distance of that point from the body, the apparent attraction would obey the law of inverse squares. He was unable, however, to imagine any physical cause for such a distribution of ether-pressure. The most famous theory of gravitation is undoubtedly that of the Swiss philosopher Le Sage. According to him there is an enormous number of extremely small, "ultramundane" corpuscles of some sort or other, flying about through space with tremendous speed, and in every conceiv-

able direction. If there were only one body in space it would be bombarded equally on all sides by the corpuscles, and the impact-forces exerted upon it would be in equilibrium. But Le Sage conceived that if there were *two* bodies in space, each of them would shield the other one to a certain extent, so that the bombardment that either body received would be most severe on the side remote from the other one, and hence the two bodies would be urged together, and there would be an apparent attraction between them. There are a host of objections to this theory, and we cannot even momentarily consider it to be true. For example, in order to explain why a great amount of *heat* is not produced by the collisions, we have to assume that the corpuscles rebound with undiminished energy. But in that case, although the bodies would still shield each other, as before, from the impact of corpuscles coming directly from the depths of space, we must note that each body would also *reflect* corpuscles in all directions, so that its neighbor would be struck by a certain number of corpuscles that would otherwise have missed it; and it has been shown that the impact against one body of the corpuscles reflected from the other one would just suffice to annul the effect of the direct shielding action, and to prevent the realization of any gravitative tendency whatever. Le Sage's original theory can be modified so as to avoid this difficulty, but it will hardly be profitable for us to discuss such modifications, because there are so many other objections to the theory that it now has only a historic interest. For example, in order to account for the fact that gravitative action varies as the *mass* of a body, and not as its *surface*, we have to suppose that the "ultramundane corpuscles" can pass through ordinary matter quite freely, so as to strike all its molecules with substantially the same frequency; and this implies a more open structure of matter than we can readily reconcile with what we know of the sizes of molecules, and of intermolecular distances. The "ether-squirt" theory of gravitation assumes that each particle of matter is a sort of center at

which ether is continuously created, so that from every such particle a ceaseless stream of ether flows out in all directions. Such a state of things would give rise to an apparent attraction, similar to gravitation; but as the theory requires us to admit a wholesale and perpetual production of ether from nothing, we must conclude that the probability of its truth is no greater than the euphony of its name. Similar remarks apply to the "ether-sink" theory, which differs from the one we have just considered only in assuming that at each molecule there is a *destruction* of ether, instead of a creation of it. The so-called "vibratory theory" of gravitation is more interesting than any that we have yet considered. You will remember that I said that the ether is believed to be incapable of transmitting waves of compression and rarefaction (analogous to sound-waves), because no phenomena could be discovered which could be attributed to such waves. It has been suggested that *gravitation* may transpire to be the missing phenomenon, and that the attraction between two bodies may be due to the mutual action of the compression-waves and rarefaction-waves that emanate from them. Considerable attention has been paid to this hypothesis, both mathematically and experimentally. It has been shown that a tuning-fork vibrating in the air can attract a light pith ball, and other phenomena of a like nature have been observed. The mathematical investigations that the theory calls for are exceedingly difficult, and I am not aware that they have yielded any conclusive results. It appears to be true, however, that a particle would be attracted toward the center of disturbance if its density were greater than that of the surrounding medium, and its dimensions small in comparison with the length of the waves. This result, so far as it goes, is favorable to the wave-theory; for matter is universally admitted to be denser than ether, and there is good reason for believing that if gravitation-waves exist at all, they are very long. In connection with this theory Lord Kelvin has called attention to "the general principle that in fluid motion the

average pressure is least where the average energy of motion is greatest." Now if the wave-theory of gravitation is true, the vibratory energy of the ether would be greatest in the immediate neighborhood of molecules of matter; and hence the ether-pressure would be least at such places, and we should have a distribution of pressure something like that demanded by Newton's theory of gravitation. The wave-theory is quite interesting, but unfortunately there are certain grave objections to it, some of which appear to be absolutely fatal. In the first place the theory requires us to admit that a body exerts a greater attractive power when hot than it does when cold; because when the body is hot its molecules are vibrating more energetically, and hence the waves that they emit have a greater amplitude. No such phenomenon has ever been detected. Again, if gravitative attraction is due to a wave-motion in the ether, we should have to admit that it has a finite speed of propagation. Nothing of the kind has been observed; but we know from astronomical considerations that if there is any such a finite speed of propagation, it is certainly greater than a million times the speed of light. This naturally suggests that gravitation is *not* due to any sort of wave-motion in the medium that transmits light. In Maxwell's theory of gravitation it is assumed that bodies produce a stress in the ether about them, of such a nature that there is a *pressure* along the lines of gravitative force, combined with an equal *tension* in all directions at right angles to those lines. (In the case of a single body in space, the pressures would be radial, and the surfaces of equal tension would be concentric spheres described about the body as a center; the stresses in the ether about the body being somewhat similar to those that exist in a cannon at the moment of discharge.) "Such a state of stress," says Maxwell, "would no doubt account for the observed effects of gravitation. We have not, however, been able hitherto to imagine any physical cause for such a state of stress. It is easy to calculate the amount of this stress which would be

required to account for the actual effects of gravity at the surface of the earth. It would require a pressure of 37,000 tons' weight on the square inch in a vertical direction, combined with a tension of the same numerical value in all horizontal directions. The state of stress, therefore, which we must suppose to exist in the invisible medium, is 3,000 [1,000] times greater than that which the strongest steel could support." * Maxwell's theory is somewhat promising, but I think we cannot say more than this of it until a sufficient cause for the ether-stresses can be found. We may now pass to the consideration of Lord Kelvin's vortex-theory of the constitution of molecules; and here we find that there is some small hope of explaining gravitation, though it is of a purely negative character. It is known that vortices exert a sensible influence upon one another, even when they are a considerable distance apart, and for certain special cases this influence has been investigated with a considerable approach to precision; but the vortex-theory has not yet been developed sufficiently to enable us to investigate the interaction of vortices with *absolute* precision, and there are, undoubtedly, certain residual effects which are not included in the approximate equations that form the basis of what we now know about vortices.† It is possible that these neglected residual effects will prove to be sufficient to account for gravitative attraction; for gravitation, as is well known, is an extremely weak force, becoming sensible only when bodies of enormous size are involved. The difficulty of deciding this point is tremendous, and at present we can only say that the vortex-theory may *possibly* be competent to explain gravitation. Professor Thomas Preston makes an interesting suggestion about gravitation, which I will quote to you, although I do not think it is put forward as being in any degree probable. I have told you

* *Encyclopædia Britannica*, article *Attraction.*

† For a mathematical discussion of the interaction of vortices, see Professor J. J. Thomson's *Treatise on the Motion of Vortex Rings* (London, Macmillan & Co., 1883).

that a finite ether-vortex must either return into itself so as to form a closed curve, or must have its ends against a bounding surface of the ether. Thus it would be possible to have vortices that do not return into themselves, but which have ends that abut against molecules of dense matter. With this possibility in mind Professor Preston says, "We might suppose a body connected to the earth by vortex filaments in the ether, which would replace the lines of force. The ether is spinning round these lines, and when the body is lifted from the earth the work done is expended in increasing the length of the vortex filaments. The work is thus being stored up as energy of motion of the ether, and when the body falls to earth the vortex lines diminish in length, and their energy of motion passes into the body and is represented by the kinetic energy of the mass."* Professor Preston probably intended this suggestion as a mere illustration of the *possibility* of explaining gravitation; for it would be quite extravagant to imagine every molecule in the universe to be united to every other one by a vortex filament — space could hardly contain such a tangle. Moreover, since vortices cannot intersect, a few seconds of intermolecular motion would suffice to tie up the vortex-system into a mass of knots that would drive Gordius mad with envy, and render the "first law of motion" impossible. Dr. Burton, in connection with his strain-figure theory of the constitution of molecules, has suggested that molecules do not have definite sizes, but that in the ether surrounding each molecular center there are stresses and strains which grow continually less as we pass away from that center, but which never absolutely vanish. In this case every molecule in the universe would exert *some* influence on every other molecule. Dr. Burton shows that in its most general form his theory could account for either attraction or repulsion, but that by making a certain very simple assumption about the nature of the strain-figures, the theory could be

* Thomas Preston, *Theory of Heat* (London and New York, Macmillan & Co., 1894), page 90.

modified so that the forces acting between distant molecules should always be attractive; yet even if the strain-figure theory should afford a perfectly satisfactory explanation of gravitation, we could not logically accept that explanation until the fundamental conceptions of the original hypothesis were shown to be in harmony with all the other phenomena of matter. I have now reviewed, briefly, some of the more famous and interesting theories that have been proposed to account for gravitative attraction, and it is easy to see that they all fail in some important particular. It may be that the future will bridge over some of these failures. It may be, on the other hand, that we have been looking at the problem from the wrong point of view, altogether.

Conclusion. — We have examined the molecular theory of matter as it stands to-day, and we have found that something is known of the constitution of gases, a little about the constitution of liquids, and almost nothing, for certain, of solids. So far as the sizes of molecules are concerned, we have seen that it is possible to discover the general *order* of their magnitude; and we have also seen that nothing whatever is known about their constitution, or about the mechanical nature of intermolecular forces. We are still very far from having a complete theory of matter — our knowledge of it is in fact very fragmentary — and yet there is strong reason to believe that we are working in the right direction. A great deal has been done in the last forty years, and it is just possible that within the next forty the world will be fortunate enough to produce a great genius who shall coördinate the isolated facts that we now have, fill up the vast gaps in our present knowledge, and provide us with a classical treatise on *The Constitution of Matter*, which shall be worthy to stand on our shelves beside the immortal *Principia* of Sir Isaac Newton.

APPENDIX.

On the Integration of Certain Equations in the Text. — In deriving equations (2) and (4), and in constructing the table on page 26, it is necessary to perform certain integrations that will doubtless prove troublesome to the student unless he has devoted more time to the integral calculus than is usual in our colleges and scientific institutions. The processes by which these integrations may be effected will therefore be briefly indicated. It is easily shown, by direct differentiation, that

$$d\left(x^{n-1}\cdot\epsilon^{-x^2}\right)=(n-1)\,x^{n-2}\cdot\epsilon^{-x^2}\,dx-2\,\epsilon^{-x^2}\cdot x^n dx.$$

If we integrate this equation, term by term, and then transpose and divide by 2, we have the formula

$$\int\epsilon^{-x^2}\cdot x^n dx=-\tfrac{1}{2}x^{n-1}\cdot\epsilon^{-x^2}+\frac{n-1}{2}\int x^{n-2}\cdot\epsilon^{-x^2}dx. \quad (61)$$

By successive applications of this formula any integral having the form of the left-hand member of (61) can be made to depend upon another integral of the same form, but with the exponent of x unity (if n is odd) or zero (if n is even). Hence every integral of this form depends, ultimately, on one or other of the two following forms:

$$\int\epsilon^{-x^2}\,x\,dx, \qquad \text{or} \quad \int\epsilon^{-x^2}\,dx. \quad (62)$$

The first of these is immediately integrable; for if we multiply it by -2 it becomes

$$\int\epsilon^{-x^2}\,d\left(-x^2\right)=\epsilon^{-x^2}.$$

The second one is much more difficult to handle, and we may distinguish two cases — (1) when the limits of the integration are both either infinite or zero, and (2) when one (or both) of them is a finite quantity other than zero. If the limits are 0 and ∞ the integration may be effected by the following artifice. Consider the surface whose equation is

$$z = \epsilon^{-(x^2+y^2)}. \tag{63}$$

The volume included between this surface and the plane $z=0$, and between the x-limits 0 and ∞, and the y-limits 0 and ∞, is

$$V = \int_0^\infty \int_0^\infty \epsilon^{-(x^2+y^2)} dx\, dy. \tag{64}$$

If we represent the integral

$$\int_0^\infty \epsilon^{-x^2} dx \tag{65}$$

by u, then, integrating (64) with respect to x, we have

$$V = u \int_0^\infty \epsilon^{-y^2} dy. \tag{66}$$

Now the integral expressed in (66) is evidently the same as (65), since its value cannot depend upon the particular symbol that we use to represent the variable quantity. But we have represented the value of (65) by u; and hence (66) becomes

$$V = u^2. \tag{67}$$

If we now return to (63), and express the value of z in *polar* coördinates, we have

$$z = \epsilon^{-r^2}$$

(since $x^2+y^2=r^2$). The elementary area in the plane $z=0$ becomes $rd\theta \,.\, dr$ instead of $dxdy$, and the limits of the integration (in order to include the same part of the solid as

before) are 0 and ∞ for r, and 0 and $\frac{1}{2}\pi$ for θ. Hence the volume of the solid, expressed in polar coördinates, is

$$V = \int_0^\infty \int_0^{\frac{\pi}{2}} \epsilon^{-r^2} r d\theta dr. \tag{68}$$

Integrating with respect to θ we have

$$V = \frac{\pi}{2}\int_0^\infty \epsilon^{-r^2} rdr. \tag{69}$$

This integral has the same form as the first of the expressions in (62), and hence we have

$$\int_0^\infty \epsilon^{-r^2} rdr = -\tfrac{1}{2}\epsilon^{-r^2}\Big]_0^\infty = -\tfrac{1}{2}(\epsilon^{-\infty} - \epsilon^{-0})$$

$$= -\tfrac{1}{2}(0-1) = \tfrac{1}{2}; \tag{70}$$

and therefore, from (69),

$$V = \frac{\pi}{4}.$$

Equating this value of V with that given in equation (67), we have

$$u^2 = \frac{\pi}{4}, \qquad \text{or } u = \tfrac{1}{2}\sqrt{\pi} = 0.8862269...,$$

which is therefore the value of (65).

Returning now to the integral

$$\int \epsilon^{-x^2} x^n dx, \tag{71}$$

let us make successive applications of equation (61), until the exponent of x has been reduced to either unity or zero (according as n is odd or even). We shall then have (71) expressed as a series, whose terms, with the exception of the last one, will all be of the form

$$Ax^m \epsilon^{-x^2}.$$

Evidently this expression is zero when $x=0$, and it can be shown, by the usual methods employed in the differential calculus for evaluating indeterminate quantities, that it is also zero when $x=\infty$. Hence when (71) is integrated between the limits 0 and ∞ all the terms of the series obtained by successive applications of (61) disappear, with the exception of the last one, which is

$$\frac{(n-1)(n-3)(n-5)\dots 2}{2^{\frac{n-1}{2}}}\int_0^\infty \epsilon^{-x^2}\,x\,dx \tag{72}$$

when n is odd, and

$$\frac{(n-1)(n-3)(n-5)\dots 1}{2^{\frac{n}{2}}}\int_0^\infty \epsilon^{-x^2}\,dx \tag{73}$$

when n is even. We have already found that the value of the integral in (72) is $\frac{1}{2}$ [see equation (70)], and that the value of that in (73) is $\frac{\sqrt{\pi}}{2}$. Hence, finally,

$$\int_0^\infty \epsilon^{-x^2}x^n\,dx=\left\{\begin{array}{l}\dfrac{(n-1)(n-3)\dots}{2^{\frac{n+1}{2}}}\ \text{(if n is odd),}\\[2ex] \dfrac{(n-1)(n-3)\dots}{2^{\frac{n+2}{2}}}\sqrt{\pi}\ \text{(if n is even).}\end{array}\right\} \tag{74}$$

These expressions have several applications in the text. If, for example, we put $v=ax$ in the equation immediately following (3), on page 25, we have

$$k=\frac{2Nma^2}{\sqrt{\pi}}\int_0^\infty \epsilon^{-x^2}x^4dx.$$

Here the exponent of x is even, and by applying the second of the values given in (74) we have

$$k=\frac{2Nma^2}{\sqrt{\pi}}\cdot\frac{3\times 1}{2^3}\cdot\sqrt{\pi}=\frac{3}{4}Nma^2,$$

as in equation (4). Again, if we put $v = ax$, the second expression after (1), on page 24, becomes

$$\frac{4Na}{\sqrt{\pi}}\int_0^\infty \epsilon^{-x^2}\, x^3 dx.$$

Here the exponent of x is odd, and applying the first of the values given in (74) we find that the expression under consideration becomes

$$\frac{4Na}{\sqrt{\pi}}\cdot\frac{2}{2^2} = \frac{2Na}{\sqrt{\pi}},$$

and hence

$$V_0 = \frac{2a}{\sqrt{\pi}},$$

as in equation (2).

In order to integrate (1) between given *finite* limits, we may first put $v = ax$, as before, and then expand the exponential function in accordance with the formula

$$\epsilon^w = 1 + w + \frac{w^2}{1.2} + \frac{w^3}{1.2.3} + \dots,$$

after which the integration may be performed term by term. The series thus obtained is

$$\frac{4N}{\sqrt{\pi}}\left\{\frac{x^3}{3} - \frac{x^5}{5} + \frac{x^7}{14} - \frac{x^9}{54} + \frac{x^{11}}{264} - \frac{x^{13}}{1560} + \frac{x^{15}}{10800} - \dots\right\}. \quad (75)$$

Performing the integration between the limits $v = 0$ and $v = mV_0$ (see page 26) is the same thing as performing it between the limits $x = 0$ and $x = \frac{mV_0}{a}$ $\left(\text{since } x = \frac{v}{a}\right)$. By referring back to equation (2) we see that

$$\frac{mV_0}{a} = \frac{2m}{\sqrt{\pi}};$$

and it was by substituting this quantity in (75) that the table on page 26 was calculated for the values $m = \frac{1}{4}$ to $m = 1$, inclusive. When m is much greater than unity (75) con-

verges so slowly that it is no longer useful for calculation. For higher values of m we therefore develop the integral in (1) in a different manner. If we first put $v = ax$, as before, and then integrate by parts once, in accordance with (61), the integral of equation (1), between the limits 0 and x, becomes

$$\frac{2N}{\sqrt{\pi}}\left\{\int_0^x \epsilon^{-x^2}\,dx - x\epsilon^{-x^2}\right\}. \tag{76}$$

Now we have, in general,

$$\int_0^x X dx = \int_0^\infty X dx - \int_x^\infty X dx,$$

where X is any continuous function of x; and hence

$$\int_0^x \epsilon^{-x^2}\,dx = \int_0^\infty \epsilon^{-x^2}\,dx - \int_x^\infty \epsilon^{-x^2}\,dx. \tag{77}$$

By substituting in (76) and remembering that the value of the first integral in the second member of (77) is $\frac{1}{2}\sqrt{\pi}$, the integral of (1), between the limits 0 and x, becomes

$$\frac{2N}{\sqrt{\pi}}\left\{\tfrac{1}{2}\sqrt{\pi} - x\epsilon^{-x^2} - \int_x^\infty \epsilon^{-x^2}\,dx\right\}. \tag{78}$$

By successive applications of (61), we may develop the integral in (78) in terms of descending powers of x. Thus:

$$\int_x^\infty \epsilon^{-x^2}\,dx = \epsilon^{-x^2}\left\{\frac{1}{2x} - \frac{1}{4x^3} + \frac{3}{8x^5} - \frac{15}{16x^7} + \dots\right\}. \tag{79}$$

This series is apparently divergent, but it can easily be shown that the sum of all the terms after the nth term is less than the nth term multiplied by ϵ^{-x^2}; and hence, in applying (79), we should compute the series until its terms begin to increase; and if we preserve the terms only up to this point the result will be very close to the true value of the integral, when x is

large. By substituting (79) for the integral in (78), the integral of (1) between the limits 0 and x is found to be

$$N\left\{1-\frac{2\epsilon^{-x^2}}{\sqrt{\pi}}\left(x+\frac{1}{2x}-\frac{1}{4x^3}+\frac{3}{8x^5}-\frac{15}{16x^7}+\ldots\right)\right\}.$$

This expression converges rapidly for large values of x, and it was used in computing the values given in the table on page 26 for $m=2$, 3, and 4, and also for computing the numbers mentioned on page 27. As explained above, the value of x corresponding to any given value of m is $\frac{2m}{\sqrt{\pi}}$.

Rankine's Method for Calculating the Ratio of the Specific Heats of Gases. — It is not easy to measure the specific heat of a gas at constant *volume*, and hence the ratio of the specific heats is usually obtained by some indirect process. If the specific heat at constant *pressure* is known, this ratio may be determined by the following method. Conceive a unit weight of gas to be confined in a vertical cylinder provided with a piston. Let V_1 be the volume of the gas, and t_1 its absolute temperature. With the piston *fixed* (so that V_1 cannot change) let the gas be heated until its temperature becomes t_2. The quantity of heat required to effect this change will be

$$S_v\,(t_2-t_1),$$

where S_v is the specific heat of the gas at *constant volume;* and multiplying this expression by J (the mechanical equivalent of heat) we find that the mechanical energy required to effect the change in temperature is

$$JS_v\,(t_2-t_1). \tag{80}$$

Now let us conceive that instead of heating the gas at constant *volume,* we raise its temperature through the same range as before, but with the *pressure* of the gas constant. This can be effected by loading the piston with a known weight, and allowing the gas to expand by pushing the weight before

it. The amount of energy required to raise the temperature of the gas from t_1 to t_2 under the new conditions will be

$$JS_p(t_2 - t_1), \tag{81}$$

where S_p is the specific heat of the gas at constant *pressure.* Now (81) will be greater than (80), because the gas, in expanding, does work in raising the weight. Moreover, a certain amount of energy is required to separate the molecules of the gas against the attractions that they exert upon one another. The experiments of Joule and Thomson have shown that this last quantity is very small for the "permanent gases," and in the present calculation we shall neglect it, and assume that the difference between (80) and (81) is due solely to the external work that the gas does in pushing up the weight. If the weight is such that the gas exerts a pressure P against each unit area of the cylinder and piston, the external work done will be

$$P(V_2 - V_1),$$

where V_1 and V_2 are the initial and final volumes, respectively. Hence, returning to (80) and (81), we have

$$JS_p(t_2 - t_1) = JS_v(t_2 - t_1) + P(V_2 - V_1), \tag{82}$$

or, dividing by $J(t_2 - t_1)$,

$$S_p = S_v + \frac{P(V_2 - V_1)}{J(t_2 - t_1)}. \tag{83}$$

Now the characteristic gas-equation gives us

$$PV_2 = Rt_2 \quad \text{and} \quad PV_1 = Rt_1,$$

and hence, subtracting and dividing by $(t_2 - t_1)$,

$$\frac{P(V_2 - V_1)}{(t_2 - t_1)} = R.$$

Making this substitution in (83), we have

$$S_p = S_v + \frac{R}{J}, \tag{84}$$

from which the ratio of the specific heats can be determined, if either of them is known. Thus if S_p is known, we have, from (84),

$$\frac{S_v}{S_p}=1-\frac{R}{JS_p}. \tag{85}$$

To compute R for any given gas we must know the volume (V_0) of a unit weight of the gas at some definite temperature and pressure — say at τ_0 and P_0. Then

$$R=\frac{P_0V_0}{\tau_0}, \tag{86}$$

and (85) becomes

$$\frac{S_v}{S_p}=1-\frac{P_0V_0}{J\tau_0S_p}. \tag{87}$$

The computation is given below, in tabular form, for five of the so-called "permanent gases." In this table V_0 is the volume of a gramme of the gas (expressed in cubic centimeters), this volume being measured at the freezing point of water ($\tau_0=273.1°$ C.), and under a pressure (P_0) of 1033.3 grammes per square centimeter. I have used Griffiths's value of J; that is, I have assumed that 4.27×10^4 centimeter-grammes of energy will raise the temperature of one gramme of water from 0° C. to 1° C.

Computation of $\frac{S_p}{S_v}$ for H, O, N, CO, and CO_2.

Gas	V_0	$\frac{P_0V_0}{\tau_0J}$ (= Q)	S_p	$\frac{Q}{S_p}$	$\frac{S_v}{S_p}$	$\frac{S_p}{S_v}$
Hydrogen . . .	11,157.6	0.9887	3.4090	0.2900	0.7100	1.408
Oxygen . . .	699.0	0.0619	0.2175	0.2848	0.7152	1.398
Nitrogen . . .	795.6	0.0705	0.2438	0.2893	0.7107	1.407
Carbon monoxide	809.6	0.0717	0.2438	0.2942	0.7058	1.417
Carbon dioxide .	505.4	0.0448	0.2169	0.2065	0.7935	1.260

I have also computed the ratio of the specific heats of certain vapors by the same process; and although we cannot

properly neglect the effects of inter-molecular attractions in such cases, the results obtained by applying equation (82) will be sufficiently accurate for the purpose for which we require them — namely, for computing the value of K, in equation (41). The ratios of the specific heats, as obtained by this process for the first three of the vapors in the table on page 101, are as follows: For water-vapor, $\gamma = 1.296$; for alcohol, $\gamma = 1.103$; and for bisulphide of carbon, $\gamma = 1.198$. For mercury vapor I have used the value of γ given by the experiments of Kundt and Warburg on the velocity of sound in that vapor — namely, $\gamma = 1.66$.

Plateau's "Liquide Glycérique." — Following is a translation of M. Plateau's observations on this subject: * "The films obtained from a simple solution of soap have very little persistence unless they are protected by a glass shade. A soap bubble four inches in diameter rarely lasts two minutes in the free air of a room, and usually it bursts in one minute, or even in half a minute. It was therefore important . . . to discover some better liquid; and in following out an idea suggested by M. Donny, I have been fortunate enough, after a number of trials, to obtain a liquid which gives films of remarkable persistence. It consists in a mixture of glycerine and a solution of soap, and I call it the 'glycerine liquid'. . . Let us describe the preparation of the liquid. In the first place, it ought to be prepared in summer, at a time when the temperature of the room, during the day, at least, does not fall below 20° C. [68° Fahr.]; for at temperatures much lower than this the results are poor. Marseilles soap is recommended, and my experience indicates that the best glycerine for the purpose is that made in England and known as 'Price's glycerine'. I shall assume, in what follows, that these substances are used, and that the operations are conducted at the proper temperature. It is not impossible to succeed with

* Plateau, *Statique Expérimentale et Théorique des Liquides*, Vol. I, page 161.

other soaps and other glycerines, but then the proportions must be changed, and I can give no general rule for them. The process of preparation will vary somewhat, according to what it is desired to accomplish. In the first place, if the experimenter is more desirous of simplicity of preparation than of excellence in the results, he may proceed as follows: Fresh Marseilles soap, which has retained all its moisture, is scraped into shavings and is dissolved with gentle heat in distilled water, forty parts (by weight) of water being allowed to each part of soap. When the solution has cooled to about the temperature of the room, it is filtered until the filtrate is clear. Three volumes of the clear soap solution are then put in a flask, two volumes of Price's glycerine are added, and the flask is shaken violently until its contents are thoroughly mixed. After this, it is set aside until the next day. Then, according to the quality of the Marseilles soap, it may be found that the liquid is still limpid, or that it contains a heavy precipitate. In the first case the liquid is ready for use, and the maximum duration of a four-inch bubble blown with it will be about an hour and a half; but the liquid will gradually lose its property of yielding persistent films, and after a fortnight a four-inch bubble blown with it will last only about ten minutes. In the second case the precipitate, at first held in suspension throughout the liquid, will rise toward the surface with extreme slowness, and after some days it will gather into a layer sharply separated from the rest of the solution. The clear liquid is then drawn off by means of a siphon provided with a side tube for starting the flow, and the preparation is completed. I ought to add that when the short branch of the siphon is introduced, a portion of the deposit is carried down by it, and adheres to the exterior surface of the tube in the form of a sort of reversed cone; and before filling the siphon this adherent deposit should be removed. To effect the removal the apparatus should first be left to itself for a quarter of an hour, after which the siphon should be slightly agitated in a horizontal direction.

The cone of deposit will then come away in little lumps, which gradually float upward and join the layer of deposit above. The liquid obtained in this way is much better than the preceding one. It is ready for use as soon as drawn off by the siphon, and four-inch bubbles blown with it have a maximum persistence of three hours. It will remain in good condition for nearly a year. . . . If the experimenter is willing to devote more care to the process of preparation, a far better liquid may be obtained in the following manner: After having prepared the solution of soap as before, 15 volumes of it are intimately mixed with 11 volumes of Price's glycerine, and the resulting liquid is allowed to stand for seven days. During this time a precipitate may form, or the liquid may remain clear, according to the quality of the soap; but the subsequent treatment is the same in either case. On the morning of the eighth day the flask containing the mixture is immersed in water which has been cooled to about 3° C. by shaking it with small pieces of ice, and the temperature is maintained at this point for six hours by adding ice from time to time. If the mixture of glycerine and soap solution is to be prepared in any considerable quantity, it is better to divide it among several flasks, in order that it may sooner acquire the temperature of the bath. During the prolonged action of the cold, an abundant precipitate will be produced. When the six hours have elapsed, the liquid is filtered through a rather porous filter-paper, and if there is much of it, several filters should be used simultaneously. It is necessary to prevent the liquid in the filters from becoming warmed, for otherwise the precipitate produced by the cold-bath would partially dissolve. For this purpose, and *before beginning the filtration*, a small, elongated bottle, filled with fragments of ice, is carefully placed in each filter, and closed with a glass stopper in order that it may have sufficient weight. This bottle should be so inclined that its side may rest against the filter, and the bottoms of all the flasks that contain the filter-funnels must also be surrounded by frag-

ments of ice. The soap solution is then removed from the cold-bath and poured immediately into the filters. The first portions of the filtrate will contain a precipitate, and they should therefore be poured back into the filters again. After this has been repeated two or three times the filtrate will become perfectly clear. It is hardly necessary to add that if the filtration requires a considerable time, it may be necessary to renew the ice in the little bottles from time to time. So far as the ice about the bottoms of the flasks is concerned, it may be said that the only purpose that it subserves is to prevent the first portions of the filtrate (which are poured back upon the filters) from becoming warm, and that it is no longer necessary when the filtrate has become clear. When the filtration is complete, the filtrate is allowed to stand for ten days, after which it is ready for use. With a liquid prepared in this manner, a four-inch bubble, under the most favorable conditions, may last as long as eighteen hours." Marseilles soap is a mixture of oleate, stearate, and margarate of soda, and Plateau considered that the precipitate thrown down by cold consists of the last two of these substances. He found that if pure oleate of soda is used in place of the soap, the precipitate is not formed; and he obtained a four-inch bubble, from an oleate solution, which lasted over twenty-four hours. Plateau insists strongly on the *proportions* that he gives.

On the Thermal Phenomena Produced by Extending a Liquid Film. — In the *Proceedings* of the Royal Society for 1858, Lord Kelvin has shown that certain thermal changes occur when the area of a liquid film is increased; and on pages 144 and 145 of the present volume these changes are taken into account, in computing the sizes of molecules by the surface tension method. It will be convenient, in investigating these thermal phenomena, to consider the behavior of a liquid *film* — such a film, for example, as that shown in Fig. 33. Let us suppose that at a given instant the absolute temperature

of this film is τ, the surface tension being S, and the total area of the film (counting both sides) being A. It is known that S varies with τ, and it is also known that *so long as* τ *remains constant,* S does not vary with A. It may be, however, that τ tends to vary with A; and in such a case, unless special care were taken to maintain a constant temperature by the addition or abstraction of heat from without, we should find an apparent connection between S and A, when no direct connection between them really exists. In studying the thermal phenomena of films we have therefore to consider two general cases: (1) when A varies *adiabatically* — that is, without absorbing or giving up heat, as such, to external bodies, — and (2) when A varies *isothermally*, its constancy of temperature being maintained by the addition or abstraction of heat by means of some external agency. Let us first consider the adiabatic change of A. Assuming that the temperature, τ, *does* vary during adiabatic extension, it is plain that the increase of τ, per unit increase of A, is represented by the differential coefficient $\left(\frac{d\tau}{dA}\right)$, whose value, as yet, is quite unknown. This being the increase of τ per unit increase of A, it is also plain that when A increases by an amount dA, the increment of τ will be

$$d\tau = \left(\frac{d\tau}{dA}\right) \cdot dA; \tag{88}$$

and the amount of energy appearing as sensible heat will be

$$h \cdot d\tau = h \cdot \left(\frac{d\tau}{dA}\right) \cdot dA, \tag{89}$$

where h is the quantity of energy required to raise the temperature of the entire film 1°. If, now, we wished to extend the film *isothermally*, we should have to subtract from it, for each dA of increase in area, the quantity of heat-energy that is represented by (89). The amount of *mechanical* energy expended upon the film in extending it an amount dA against the surface tension, S, would be

$$S \cdot dA; \tag{90}$$

and hence the total increase, dw, of the energy of the film would be the difference between (90) and (89), and we should have

$$dw = S \cdot dA - h \cdot \left(\frac{d\tau}{dA}\right) \cdot dA.$$

Upon dividing this expression by dA we have

$$\frac{dw}{dA} = S - h \cdot \left(\frac{d\tau}{dA}\right), \tag{91}$$

which is the total increase in the energy of the film, *per unit increase of A*. The differential coefficient in the right-hand member of (91) might be found by direct experiment, but it is more convenient to express it, by Lord Kelvin's method, in terms of another quantity whose value can be found with less difficulty. To effect the transformation in question, consider the film in Fig. 33 to be the working-body of a heat engine, and conceive it to pass through the following infinitesimal cycle: (1) It is extended by an amount ΔA, the heat produced during this extension being removed so that the process is isothermal; (2) the film is then further extended, adiabatically, by an infinitesimal amount, dA, the temperature increasing, at the same time, by an amount $d\tau$; (3) the film is then allowed to contract, isothermally, to such a point that the fourth stage in the cycle shall cause it to return to its initial condition; (4) it is then allowed to contract adiabatically, until the cycle is completed. If a diagram of this cycle be drawn on paper, with film-areas as abscissæ and surface-tensions as ordinates, the isothermals will be straight lines parallel to the axis of abscissæ, and the cycle, being infinitesimal, may be regarded as a parallelogram. The length of the parallelogram will be ΔA, and its height will be

$$\left(\frac{dS}{d\tau}\right) \cdot d\tau,$$

this being the change which S undergoes when the temperature increases by $d\tau$. The amount of mechanical energy gained in

the cycle will be represented by the area of the parallelogram; that is, it will be

$$\Delta A \cdot \left(\frac{dS}{d\tau}\right) \cdot d\tau. \tag{92}$$

The quantity of heat abstracted from the film during the first stage of the cycle is

$$h \cdot \left(\frac{d\tau}{dA}\right) \cdot \Delta A, \tag{93}$$

as we see by comparison with equation (88); and the quantity added to it during the third stage differs from (93) by only an infinitesimal amount. The thermodynamic efficiency, E, of the film, is therefore found by dividing (92) by (93); and we have

$$E = \frac{\left(\frac{dS}{d\tau}\right)}{\left(\frac{d\tau}{dA}\right)} \cdot \frac{d\tau}{h}.$$

But since the cycle under consideration is reversible, the efficiency must also be expressible by "Carnot's formula"; and hence

$$E = \frac{d\tau}{\tau}.$$

Upon equating these two values of E we find that

$$\left(\frac{d\tau}{dA}\right) = \frac{\tau}{h} \cdot \left(\frac{dS}{d\tau}\right).$$

Substituting this in (91) we find that the total increase in the energy of the film, per unit of isothermal increase in area, is

$$S - \tau \cdot \left(\frac{dS}{d\tau}\right).$$

This may be written in the form

$$\left(1 - \frac{\tau}{S} \cdot \frac{dS}{d\tau}\right) \cdot S,$$

where the parenthesis is the quantity represented by m on page 144. The computation of m for the four liquids discussed on page 145 is presented below in tabular form.

COMPUTATION OF m FOR VARIOUS LIQUIDS, AT 20° C.

LIQUID	S	$\frac{dS}{d\tau}$	m
Water	.074	—.000143	1.57
Alcohol	.026	—.000121	2.36
Bisulphide of Carbon	.033	—.000131	2.16
Mercury	.551	—.00032	1.17

The value of $\frac{dS}{d\tau}$ for water is given by the experiments of Mr. T. Proctor Hall, mentioned on page 95 of this volume. The corresponding values for alcohol, bisulphide of carbon, and mercury, were obtained by assuming (1) that the surface tension is a linear function of the temperature, and (2) that it vanishes at the critical temperature, where the liquid becomes indistinguishable from its vapor. The critical temperature of mercury is not known; but by comparing the specific heat of this liquid with the value of W given on page 101, the critical temperature was inferred to be in the neighborhood of 1,700° C.

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